STUDIES ON INORGANIC ION-EXCHANGERS AND DETERMINATION OF SUBSTANCES

SUMMARY

THESIS SUBMITTED FOR THE DEGREE OF

Doctor of Philosophy

IN

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SUMMARY

A B S T R A C T

The thesis entitled "Studies on inorganic ion-exchangers and determination of substances" comprises of six chapters. The first chapter deals with the general introduction covering a critical review of the earlier work done in this field. The literature survey has been mentioned upto 1979. A table has been given in parts a, b and c to arrange the earlier work in a concise manner. The important aspects of analytical chemistry in general and the processes that involve ion-exchange in particular have also been dealt with.

In the second chapter the preparation, physical properties, ion-exchange properties and electron exchange properties have been described. The material, zirconium phosphoiodate, has been synthesised by mixing 0.1M of zirconium oxychloride, phosphoric acid and potassium iodate in equal ratio. The presence of iodate within the channels gave the exchanger an electron exchange property which was applied for the oxidation of small amounts of iron(II), As(III), Sn(II), Ti(III) and Sb(III) to their higher valence states. The results obtained were quantitative. The mechanism has been discussed and is based on redox potential of iodate/iodide and the redox couple of the reactants under experiment.

The third chapter describes the preparation of a new ion-exchanger, zinc silicate. A complexing agent, PAN (1-(2-pyridyl-azo)-2-naphthol) has been immobilized on zinc silicate and has been studied as a chelate ion-exchanger. Properties such as ion-exchange

capacity, heat effect and stability etc. have been studied for untreated zinc silicate. PAN-sorbed zinc silicate showed greater selectivity for some metal ions; especially for Cu(II), Ni(II), Co(II) and Fe(III) and reluctance for Ag(I), Au(III) and Pt(IV). Selectivity has been determined on the basis of distribution coefficients of these metal ions. Separation of Pt(IV) from Fe(III); Au(III) from Fe(III); Ag(I) from Cu(II) and Au(III) from Cu(II) have been reported. The recovery of Pt(IV) and Au(III) from dilute solutions has also been studied.

In the fourth chapter metal ion chelation chromatography on complexone sorbed stannic silicate has been mentioned. Stannic silicate has been sorbed with complexones like xylenol orange, eriochrome black T and 1,10-phenanthroline for use as a chelate ion-exchanger. The sorption capacity for different metals has been worked out. Kd values have been determined. Xylenol orange was used for the separation of Th(IV) from Cd(II) and Zn(II); and Cu(II) from Cd(II) and Zn(II); 1,10-phenanthroline was used for the separation of Fe(II) from Fe(III). These separations are based on the stabilities of the various complexes formed by the interaction of metal ions with complexones. By elution of metal ions which forms less stable complexes with the complexones no evidence of complexing agent in the eluate was found.

The preparation, properties and application of a new chelating ion-exchanger, stannic diethanolamine, have been described in the fifth chapter. The new inorganic chelate ion-exchanger has been

synthesised by mixing of aqueous solutions of 0.1M stannic chloride and 0.4M diethanolamine. The precipitate was obtained at a definite mole ratio of the reactants. The product obtained after washing, drying etc. can be used as granules to prepare a column. The material shows selective uptake of some of the metal ions based on the coordination with lone pair of nitrogen. Separations of Hg(II) from Cu(II) and Zn(II); Pb(II) from Mn(II); Cu(II) from Fe(III) and Pt(IV); and Zn(II) from Mn(II) have been achieved quantitatively. The formation of coloured complexes is visible in the column of chelate ion-exchanger. The structure of the material is proposed and discussed. This new chelating ion-exchanger is probably the first of its kind. Many other specific organic chelate exchange resins have been reported in the literature. However, never before possibility has been explored towards inorganic chelate ion-exchangers.

In the next and the last chapter, a spectrophotometric method has been mentioned which is used for the determination of the vanadium(V) in microgram range and is based upon a new colour reaction of brucine with ammonium metavanadate. Optimum conditions have been set for the determination of λ_{max} and was found to be 365 nm. An aliquot of vanadate solution containing 25 to 400 µg of vanadium was taken and to this 1 ml of 1% brucine and 2.5 ml of 12N HCl were added. The solution was then diluted to 25 ml with distilled water and absorbance recorded at 365 nm. In cases where less amounts of vanadium were employed, the final volume was made upto 10 ml. Mole ratio is determined by Job's method and mole ratio method. A study

of interference is done and tolerance limits for certain cases are determined. Precision of the method is calculated giving standard deviation of 3 µg for a set of nine replicate determinations of 204 µg vanadium.

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C E R T I F I C A T E

This is to certify that the work embodied in this thesis is original and is suitable for submission for the award of Ph.D. degree in Chemistry.

(J.P. Rawat)

A C K N O W L E D G E M E N T

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C O N T E N T S

LIST OF PUBLICATIONS

1. Synthesis of zirconium phosphoiodate and its use as an electron-ion-exchanger.

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2. Separation and recovery of some metal ions using PAN-sorbed-zinc silicate.

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3. Metal ion chelation chromatography on complexones sorbed stannic silicate.

   J.Liq.Chromatogr., (In press).

4. Stannic diethanolamine as a new chelating ion-exchanger.

   Talanta, (Communicated).

5. Spectrophotometric determination of vanadium(V) with brucine.

   Proc.Nat.Acad.Sci., (In press).

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C H A P T E R - I

INTRODUCTION

CHAPTER - I

INTRODUCTION

Analytical chemistry deals with the development of methods for identification, separation and determination of the substances. Identification of the substances constitutes the branch qualitative analysis and determination forms the branch quantitative analysis. Generally, the separation is the pretreatment procedure for most of the determinations and sometimes for identifications. Thus all the three techniques together form the subject of chemical analysis. Chemical analysis is based upon classical and modern methods of analysis. The modern methods of analysis are divided into two broad groups viz. instrumental and non-instrumental. Instrumental techniques find their application in quite a number of interesting work being carried out today. The non-instrumental techniques too are equally important in tackling various problems and are less expensive. The non-instrumental techniques are developed mainly for achieving separations. The various methods that are employed for separation are chromatography, electrophoresis, ion-exchange, solvent extraction, ring oven techniques and dialysis etc. Berg has given a concise account of such methods in his book entitled "Physical and chemical methods of separation" (1). Ion-exchange and chromatography are most versatile techniques in the field of separation science. Now-a-days, the ion-exchange has come to be recognised as an extremely valuable technique. All over the world numerous plants are in operation for developing the separations of

inorganic, organic and biochemical mixtures. Ion-exchange is a process in which an insoluble (or immiscible) material, when comes in contact with an electrolyte solution, takes up, stoichiometrically, ions of positive or negative charge and releases other ions of like charge from the exchanger phase into the solution phase. In laboratories ion-exchangers are used as an important tool for the solution of new problems facing our industrialists and scientists. The most important application of ion-exchange is the purification of water in an age when air and water pollution is leading to an alarming situation.

A description of ion-exchange process can be cited in the most ancient literature following a paragraph written in the holy Bible. Moses (2) wrote that the bitter water can be made drinkable by using pieces of wood. Aristotle (3) stated that sea water loses parts of a salt content when filtered through certain type of soil. The ion-exchange properties of wood cellulose in the first case and that of silicates in the second case might have served to improve the taste of water. For a long period no efforts were made to cite the ancient references.

The phenomenon of ion-exchange was rediscovered by Thomson (4) and Way (5) in 1850 by the name of base exchange in soils. When soils are treated with ammonium salts, ammonium is taken up by the soil and an equivalent amount of calcium is released. It was established by Eichorn that zeolites were responsible for this exchange in soils (6). Aluminium silicate was first synthesised by

Harms and Rümpler (7). According to Lemberg (8) and Wiegner (9) the materials responsible for this phenomenon were mainly clays, zeolites, glauconites and humic acids. These discoveries led to the use of the natural materials for water softening. Ambitious Gans adopted this technique to recover gold from sea water. But his ambition remained unfulfilled because the material of this type available at that time proved to be inadequate for the purpose. Gans (10) recognized the practical utility of the ion-exchange phenomenon for water softening using natural and synthetic zeolites and clays. The exhausted bed of the ion-exchanger was regenerated by passing a concentrated solution of sodium or potassium salts. Because of plausibility of regeneration these zeolites and clays could be used over and again. Limitations of zeolites and clays were soon realized, i.e. zeolites are decomposed by acids whereas clays are difficult to handle. To overcome these limitations a search for stable ion-exchange material was started. In 1931 Kullgren (11) observed that sulphite cellulose works as an ion-exchanger for the determination of copper. An interesting discovery began in 1935 when Adams and Holmes found that crushed phonograph records exhibit ion-exchange properties. This remarkable effect led the inventors to the synthesis of organic ion-exchange resins which had much better properties than any of the previous products (12). Various improvements were made in these resins, mainly after world war II by companies in U.S.A. and England. These resins are stable towards acids and easy to handle. The structure can be varied as desired, therefore, the difficulties observed with zeolites and clays were removed by the introduction of resins. Since then

these organic ion-exchangers have been used both in laboratory and on industrial scale for separations, recoveries of metals, purification of water, concentration of electrolytes, reactions of precipitates and elucidating the mechanism of many reactions (13).

The applications of organic ion-exchange resins are also limited under certain conditions i.e. they are unstable in aqueous systems at high temperatures and in presence of the ionizing radiations. For these reasons there has been a revived interest in inorganic ion-exchangers in recent years, as they are unaffected by ionising radiations and are less sensitive to higher temperatures. The structure of these inorganic ion-exchangers is stiff, therefore, they are more selective and suitable for the separation of ions on the basis of their different sizes. For this reason they can also be used as ionic or molecular sieves. Being suitable towards ionizing radiations they can be used advantageously in reactor technology. In order to understand these applications and to improve upon them systematic fundamental studies are being persued on these materials. This new interest in inorganic ion-exchanger may be said to begin in 1945. It was first shown by Boyd (14) that columns containing finely divided zirconium phosphate supported on silica gel could be used to separate uranium and plutonium from fission products by an ion-exchange process. In addition to zirconium phosphate many other similar substances may be prepared by combining oxides of group IV with the more acidic oxides of groups V and VI of the periodic table. Synthesis and ion-exchange properties of the compounds reported so far are summarized in table 1a.

TABLE 1a

SYNTHESIS AND ION-EXCHANGE PROPERTIES OF MULTIVALENT METAL SALTS

Sl. No.	Material	Type of exchanger	Composition	Empirical formula	I.E.C. meq/g	Selectivity	References
	(1) Zirconium based ion-exchangers						
1.	Zirconium phosphate	Amorphous	P/Zr=0.5-2.1	$Zr(OH)(PO_4)$	-	Cs^+, Rb^+, K^+, Na^+,	(15 16, 17, 18,
				$ZrO(HPO_4)$		Zn^{3+}, Sr^{2+}, Ca^{2+},	19, 20, 21, 22,
				$Zr_3(PO_4)_4$		Ni^{2+}, Zn^{2+}	23, 24, 25, 26)
				$Zr(HPO_4)_2.H_2O$			
				$Zr(HPO_4)(H_2PO_4)(OH)$			
		Semi-crystalline	-	-	-	Li^+, K^+, H^+, Cs^+	
		Crystalline	-	$Zr(HPO_4)_2.H_2O$	-	Sr^{2+}, UO_2^{2+}, Ce^{3+},	
						Na^+, Cs^+, NH_4^+	
2.	Zirconium-pyrophosphate	Amorphous	P/Zr=2.0, 2.5-2.8	-	-	Cu^{2+}, Ni^{2+}, Ca^{2+},	(27, 28)
						Na^+, Fe^{2+}, Mg^{2+}	
3.	Zirconium-hypophosphate	Amorphous	Zr/P=0.57	-	-	For multivalent metals	(29, 30, 31)

TABLE 1a (Contd.)

Sl. No.	Material	Type of exchanger	Composition	Empirical formula	I.E.C. meq/g	Selectivity	References
4.	Zirconium polyphosphate	Amorphous	-	-	-	For alkali metals (in NH_4^+ form) & Fe^{3+}, Cu^{2+}, Ca^{2+}, Ba^{2+} (in H^+ form)	(32, 33, 34)
5.	Zirconium antimonate	Amorphous	-	-	-	Na^+, K^+, NH_4^+, Rb^+, Cs^+, Li^+	(35, 36)
6.	Zirconium arsenate	Amorphous	As/Zr=1.53-1.96	-	-	Cs^+, K^+, Na^+ (at pH 2.6); Na^+, K^+, Ca^+ (at pH 4.6)	(37, 38)
		Crystalline	-	$Zr(HAsO_4)_2.H_2O$	-	-	
7.	Zirconium molybdate	Amorphous	Zr/Mo=0.5-2.0	-	2.18 for K^+ 2.43 for Cs^+	-	(39)
8.	Zirconium tungstate	Amorphous	Zr/W=1.0-0.44	-	-	Cs^+, Rb^+, K^+, Na^+, Li^+	(31, 40, 41, 42)
9.	Zirconium tellurate	Amorphous	-	$Zr(H_2TeO_6).4H_2O$	2.80	-	(43, 44)
10.	Zirconium oxalate	Crystalline	-	$Zr(OH)C_2O_4H$	2.50	Na^+, Cs^+, Rb^+, K^+	(45)

TABLE 1a (Contd.)

Sl. No.	Material	Type of exchanger	Composition	Empirical formula	I.E.C. meq/g	Selectivity	References
11.	Zirconium silicate	Amorphous	-	-	3.18	Th^{4+}, Sr^{3+}, Ca^{2+}	(46, 47)
12.	Zirconium ferrocyanide	Amorphous	Fe/Zr=0.55	-	0.95	Li^{+}, Na^{+}, NH_4^{+}	(48)
13.	Zirconium oxide	Amorphous	-	$ZrO_2.4.7H_2O$	1.00	Ca^{2+}, Ba^{2+}	(49, 50)
(11)	Thorium based ion-exchangers						
14.	Thorium phosphate	Crystalline	-	$Th(HPO_4)_2.3H_2O$	3.70	-	(51, 52)
15.	Thorium arsenate	Crystalline	-	$Th(HAsO_4)_2.H_2O$	-	-	(53)
16.	Thorium molybdate	Amorphous	-	-	0.75	Fe^{3+}, Zr^{4+}, Pb^{2+}	(54)
17.	Thorium tungstate	Amorphous	Th/W=2.0	$Th(OH)_2(HWO_4)_2.nH_2O$	0.46	Cs^{+}, K^{+}, Na^{+}	(55)
(111)	Titanium based ion-exchangers						
18.	Titanium phosphate	Amorphous	P/Ti=0.6-2.0	$(TiO)_{0.535}(H_2PO_4)_{0.369}(OH)_{1.77}1.11H_2O$		-	(56, 57, 58,
				$TiH_2(PO_4)_2.4H_2O$	7.5	Cs^{+}	59, 60, 61
				$Ti_3(PO_4)_4$	-	-	62, 63)
		Crystalline	-	$Ti(HPO_4)_2.H_2O$	7.15	-	

TABLE 1a (Contd.)

Sl. No.	Material	Type of exchanger	Composition	Empirical formula	I.E.C. meq/g	Selectivity	References
19.	Titanium arsenate	Amorphous	-	$Ti(HAsO_4)_2 \cdot 2.5H_2O$	1.00	Pb^{2+}, Cu^{2+}, Ba^{2+}, Sr^{2+}, Zn^{2+}, Cd^{2+}	(64, 65, 66, 67)
		Crystalline	-	$Ti(HAsO_4)_2 \cdot H_2O$	5.80	-	
20.	Titanium antimonate	Amorphous	Sb/Ti=1.0	-	0.70	Rare earth metals	(68, 69)
21.	Titanium molybdate	Amorphous	Mo/Ti=0.5-2.0	-	0.8-1.60	Pb^{2+}, Ba^{2+}, Tl^{+}, K^{+}	(70, 71)
22.	Titanium tungstate	Amorphous	-	-	0.4-0.76	Ca^{+}, Mg^{2+}, Ca^{2+}	(71, 72, 73)
23.	Titanium selenite	Amorphous	Ti/Se=1.39	-	0.78	Cd^{2+}	(74)
24.	Titanium vanadate	Amorphous	V/Ti=4.0	$Ti_5(V_5O_9 \cdot 1.5H_2O)_4 \cdot 15H_2O$	0.68	Sr^{2+}	(75)
25.	Titanium tellurate	Amorphous	Te/Ti=2.06	-	-	-	(76)
26.	Titanium ferrocyanide	Amorphous	$Fe(CN)_6^{4-}$/Ti=2.0	-	1.40	Ca^{+}	(77)
27.	Titanium silicate	Amorphous					(78)

TABLE 1a (Contd.)

Sl. No.	Material	Type of exchanger	Composition	Empirical formula	I.E.C. meq/g	Selectivity	References
	(iv) Cerium(IV) based ion-exchangers						
28.	Cerium phosphate	Amorphous	P/Ce=1.03-1.95	$Ce_3(OH)_8(H_2PO_4)_4$	2.90	Ca^+, Rb^+, K^+, Na^+, Li^+	(79, 80, 81, 82, 83, 84)
		Micro-crystalline	P/Ce=1.5	$Ce-O-Ce(HPO_4)_3.H_2O$	-	Ca^+, Na^+, Ag^+	
		Crystalline	-	$Ce(HPO_4)_2.H_2O$	5.20	-	
29.	Cerium phosphate sulphate	Crystalline	Ce:P:S=2:1:2	$Ce_2O(HPO_4)_{3-x}(SO_4)_x.4H_2O$ where 0 x 1	-	Na^+, Ag^+, Sr^{2+}, Cs^+, Ca^{2+}	(79, 85, 86)
30.	Cerium arsenate	Micro-crystalline	As/Ce=2.0	$Ce(HAsO_4)_2.2H_2O$	4.25	-	(87, 88)
31.	Cerium molybdate	Amorphous	-	-	0.96	-	(89)
32.	Cerium antimonate	Amorphous	Sb/Ce=0.35	-	1.23	Hg^{2+}	(90)
33.	Cerium tungstate	Amorphous	Ce^{4+}/WO_4^{2-}=0.49	-	0.89	Hg^{2+}, Tl^+	(91)
	(v) Tin(IV) based ion-exchangers						
34.	Stannic phosphate	Amorphous	P/Sn=1.25-1.50	-	1.20-1.44	Cs^+, Rb^+, K^+, Na^+, Li^+, Cu^{2+}, Zn^{2+}, Ni^{2+}, Co^{2+}	(92)
		Crystalline	-	$Sn(HPO_4)_2.H_2O$	7.90	-	

TABLE 1a (Contd.)

Sl. No.	Material	Type of exchanger	Composition	Empirical formula	I.E.C. meq/g	Selectivity	References
35.	Stannic arsenate	Amorphous	Sn/As=1.8	-	0.79-0.94	Al^{3+}, Ga^{3+}, In^{3+}	(93, 94)
		Crystalline	-	$Sn(HAsO_4)_2.H_2O$	-	-	
36.	Stannic molybdate	Amorphous	Sn/Mo=1.10	-	1.00	Pb^{2+}	(95)
37.	Stannic tungstate	Semi-transparent	Sn/W=0.55	-	0.58	Co^{2+}, Ba^{2+}, Ni^{2+}, Pb^{2+}, Mn^{2+}, Cu^{2+} Sr^{2+}	(96)
38.	Stannic antimonate	Amorphous	Sb/Sn=1.0	-	0.75	Cu^{2+}, Ni^{2+}, Co^{2+}	(97)
39.	Stannic selenite	Amorphous	Sn/Se=1.33	$(SnO_4)(OH)_2(SeO_3)_3.6H_2O$	0.75	Li^+, Na^+, K^+	(98)
40.	Stannic ferrocyanide	Amorphous	Sn/Fe=3.0	$(SnO)_3.(OH)_3.HFe(CN)_6.3H_2O$	2.02	K^+, Ba^{2+}, Na^+	(99)
41.	Stannic vanadate	Amorphous	Sn/V=1.0	$(Sn(OH)_3)_3V_3O_9.4H_2O$ n	0.85	K^+, Na^+, Li^+	(100)
42.	Stannic silicate	Amorphous					(101)

TABLE 1a (Contd.)

Sl. No.	Material	Type of exchanger	Composition	Empirical formula	I.E.C. meq/g	Selectivity	References
	(vi) Chromium(III) based ion-exchangers						
43.	Chromium phosphate	Amorphous (Polyfunctional)	P/Cr=0.6-1.0	$Cr_2O_2HPO_4$ $Cr_2O(HPO_4)_2$	5.90	Na^+, K^+, Rb^+, Cs^+, Ca^{2+}, Sr^{2+}, Ba^{2+}	(102, 103)
44.	Chromium tripolyphosphate	Glassy	Cr/P=1:2.48	$Cr_5(P_3O_{10})_3.nH_2O$	-	Cs^+, Rb^+, K^+, Na^+, H^+	(104)
45.	Chromium arsenate	Amorphous	As/Cr=1.98	$Cr_2O_5(H_5AsO_4)_4.3H_2O$	0.63	Zr^{4+}, Hf^{4+}	(105)
46.	Chromium molybdate	Amorphous	Mo/Cr=1.90	$Cr_2O_5(H_2MoO_4)_4.3H_2O$	0.34	Pb^{2+}, Ga^{3+}	(105)
47.	Chromium tungstate	Amorphous	W/Cr=1.92	$Cr_2O_5(H_2WO_4)_4.11H_2O$	0.02	Th^{4+}, Hf^{4+}	(105)
48.	Chromium antimonate	Amorphous	Sb/Cr=2.95	$Cr_2O_5.3Sb_2O_5.22H_2O$	0.42	Pb^{2+}, Co^{2+}	(105)
49.	Chromium tellurate	Amorphous	Te/Cr=0.2	-	-	-	(76)
50.	Chromium Ferrocyanide	Amorphous	Cr/Fe=0.66	-	-	-	(106)
	(vii) Iron(III) based ion-exchangers						
51.	Ferric phosphate	Amorphous	P/Fe=2.0	$FeH(HPO_4)_2.nH_2O$	0.77	Pb^{2+}, Eu^{3+}, Ga^{3+}	(107)

TABLE 1a (Contd.)

Sl. No.	Material	Type of exchanger	Composition	Empirical formula	I.E.C. meq/g	Selectivity	References
52.	Ferric pyrophosphate	-	-	$Fe_4(P_2O_7)_3$	-	In^{3+}	(108)
53.	Ferric arsenate	Amorphous	As/Fe=1.33	-	0.80	K^+, Na^+, Li^+	(109)
54.	Ferric antimonate	Amorphous	Sb/Fe=2.4	-	0.82	Cd^{2+}	(110)
55.	Ferric tungstate	Amorphous	Fe/W=1.0	-	0.84	Ce^{4+}	(111)
56.	Ferric ferrocyanide	Amorphous	-	-	3.60	Ca^+	(112, 113)
57.	Ferro silicate	Amorphous					(114)
	(viii) <u>Aluminium(III) based ion-exchangers</u>						
58.	Aluminium triphosphate	-	Al/P=0.5-0.66	-	2.50	-	(115)
59.	Aluminium vanadate	-	-	$(Al_2O_3)_n(V_2O_5)_m$ n/m=2.0-0.5	-	-	(116)
60.	Aluminium antimonate	Amorphous	Al/Sb=4.2	-	1.14	Ag^+, UO_2^{2+}, Ba^{2+}, Tl^{4+}	(117, 118)

TABLE 1a (Contd.)

Sl. No.	Material	Type of exchanger	Composition	Empirical formula	I.E.C. meq/g	Selectivity	References
	(ix) Other acidic salts						
61.	Tantalum arsenate	Amorphous	Ta/As=2.8	-	1.09	Na^+, K^+, Ba^{2+}	(119)
62.	Tantalum antimonate	Amorphous	Ta/Sb=1.5	-	0.89	Na^+, K^+, NH_4^+	(120)
63.	Niobium arsenate	Amorphous	Nb/As=1.96	-	1.06	Ca^{2+}, Mn^{2+}, Al^{3+}	(121)
64.	Niobium antimonate	Semi-crystalline	Nb/Sb=1.40	-	1.10	Mg^{2+}	(122, 123)
		Crystalline	-	$Nb_2.Sb_3.O_{11}.(OH)_3.2H_2O$	0.90	NH^+	
65.	Tungsten ferrocyanide	Amorphous	W/Fe=1.32	-	1.02	-	(124)
66.	Molybdate ferrocyanide	Semi-crystalline	Fe/Mo=2.3	$(H_4Fe(CN)_6)_4(MoO_3(H_2O)_n)_{16}$	12.0	Cs^+	(125)
67.	Antimonic acid	Crystalline	-	$Sb_2O_5.4H_2O$	1.28	K^+, Li^+	(126)
68.	Uranyl hydrogen phosphate	-	-	$UO_2HPO_4.4H_2O$	-	Cs^+, Rb^+, K^+	(127)
69.	Vanadium ferrocyanide	Amorphous	V/Fe=0.93	-	2.56	Cs^+, Rb^+	(128)
70.	Bismuth tungstate	Amorphous	Bi/W=0.5	-	0.74	Pb^{2+}	(129)

TABLE 1a (Contd.)

Sl. No.	Material	Type of exchanger	Composition	Empirical formula	I.E.C. meq/g	Selectivity	References
71.	Stannous ferrocyanide	Amorphous	Sn/Fe=1.0	$SnO.H_2Fe(CN)_6.2.5H_2O$	2.03	Cu^{2+}, Ni^{2+}, Mn^{2+}	(130)
72.	Zinc ferrocyanide	Amorphous	Zn/Fe=1.98	$Zn_2Fe(CN)_6$	6.10	Cs^+	(131)
73.	Zinc silicate	Amorphous	Zn:Si 1:2	-	2.30	-	(132)
(x)	Double salts						
74.	Tin(IV) Vanado phosphate	Crystalline	-	-	-	Ba^{2+}, Cu^{2+}	(133)
75.	Zirconium phosphate silicate	Amorphous	-	-	-	-	(134)
76.	Zirconium phosphomolybdate	Amorphous	-	-	-	-	(135)
77.	Ammonium phosphomolybdate	-	-	-	-	-	(136)
78.	Lead strontium phosphate	-	-	-	-	-	(137)
79.	Tin(IV) tungsto arsenate	-	Sn:W:As 12:5:2	-	1.06	-	(138)
80.	Pyridium tungsto arsenate	-	-	$(C_5H_5NH)_5W_{12}AsO_{40}$	-	Cs^+, Ag^+	(139)
81.	Tin(IV) molybdo-arsenate	Amorphous	Sn:Mo:As 2: 1: 1	-	1.4	-	(140)

In addition to the materials mentioned so far a number of other types of exchangers have been developed. In particular, electron exchangers, redox exchangers and chelate ion-exchangers have found the highest interest of all such materials. The electron exchangers may be considered as solid oxidation and reducing agents. They contain the species forming a redox couple and after having oxidised (or reduced) a substrate the electron exchangers can be regenerated by a suitable oxidising or reducing agent. The reactivity of electron exchangers is due to built-in redox components. The most important advantage of electron exchangers over dissolved oxidising or reducing agents is their insolubility and hence an electron exchanger can be easily separated from the solution containing a substrate being oxidised or reduced. The solution is free from the contamination of any redox agent or its products. Only electrons and protons are transferred between the resin and the solution. Therefore, the only possible change in the solution, except for the redox reaction of the substrate, is a change in pH. Another advantage of electron exchangers is that they can be readily regenerated (oxidised or reduced) after use.

The electron exchangers are characterised by their redox capacity, redox potential and reaction rate. The redox capacity is the amount (in equivalents) of a substrate being oxidised or reduced by a specified amount of the exchanger. The reaction rate indicates the time required for redox process under a given set of conditions.

Redox ion-exchangers are conventional ion-exchangers which contain reversible redox couple. The redox couples are introduced in the exchanger as counter ions. The redox ion-exchangers behave, in a way, similar to electron exchangers and therefore they are also characterised by the same characteristic properties as for the electron exchangers. Many authors do not differentiate between these two and the name either the redox ion-exchanger or electron exchanger is used in general. Some of the important redox exchangers are summarised in table 1b.

TABLE 1b

REDOX ION-EXCHANGERS AND THEIR REDOX CAPACITY

Sl. No.	Name of Redox Exchanger	Redox capacity, (m.eq/g)	References
1.	Phosphomolybdo vanadic acid	0.318	(141)
2.	Tetrachlorohydroquinone	-	(142)
3.	Tetrachloroquinone	-	(143)
4.	p-benzoquinonemelamine copolymer	4.00	(143)
5.	Zirconiummolybdo vanadate	0.52	(144)
6.	Alkali and Nickel ferrocyanides	-	(145)
7.	Phosphotungsto vanadic acid	-	(146)
8.	Active carbon	-	(147)
9.	Zeolite aluminosilicate	-	(148)
10.	Zirconium peroxide meta tungstate	-	(149)
11.	Zirconium phosphoiodate	5.00	(150)

The sorption of bi- or polydentate agent on the ion-exchanger gives a new class of exchangers that is known as chelate ion-exchangers. The complexing agents form chelates with metal ions with the high degree of selectivity. Ion-exchangers of this type are mechanically and chemically more stable than the usual ion-exchangers. The chelate ion-exchangers are similar to soluble complexing agents in their complexing tendency e.g., a resin with iminodiacetic acid groups, Dowex A-1, has become commercially available as a chelate ion-exchange resin. By introduction of a suitable complexing agent it is possible to have a specific chelate ion-exchanger.

Use of ligands in chemical analysis is one of the earliest methods of determining the presence and concentration of metal ions. However, the rapid development took place only after 1945 with the introduction of ethylenediamine tetraacetic acid and related complexing (chelating) agents. Formation of a complex with a metal ion is an example of a coordination compound in which the donar of lone pair of electrons is the complexing agent and the central metal ion forms a coordinate-covalent bond with it. The formation of the complex depends upon the stability constant of the chelate formed. The interest in this field has been developed recently and such exchangers are summarized in table 1c.

TABLE 1c

SOME OF THE CHELATING ION-EXCHANGE RESINS

Sl. No.	Type of chelating resin	Sorption capacity, m.moles/g	Selectivity	Reference
1.	Oxime and diethylamine resin	2.00	Cu(II)	(151)
2.	8-hydroxyquinoline and 8-hydroxyquinadine resin	-	Cu(II) and Zn(II)	(152)
3.	O-hydroxyoxime resin	-	Mo(VI) and Cu(II)	(153)
4.	Thioglycolate resin	-	Ag(I), Bi(III), Sn(IV), Sb(III), Hg(II) from 0.1M acid; Cd(II), Pb(II), U(VI) from pH 5.5	(154)
5.	Amino acid type resin	-	U(VI), Cu(II), Ni(II) and Fe(III)	(155)
6.	Phosphate type resin	-	U(VI) and Th(IV)	(155)
7.	N-Acylphenyl-hydroxylamines	0.45	-	(156)

The studies of inorganic based chelate exchangers are meagre. Therefore, the synthesis and use of such exchangers in chemical analysis may be of importance. In the present study PAN-sorbed zinc silicate; xylenol orange, eriochrome black T and 1,10-phenanthroline sorbed stannic silicate have been synthesized and studied. A new approach has been tried to introduce the complexing agents with the matrix of the exchanger. On this basis stanniodiethanolamine has been synthesized and found to behave as a good chelating exchanger.

For a complete description of a material as an ion-exchanger the following properties must be studied:

1. The ion-exchange capacity,
2. The resistance towards acids and bases,
3. Composition,
4. Potentiometric titrations,
5. Distribution of counter ions between solution and exchanger phases,
6. Kinetics,
7. Thermodynamics, and
8. Analytical applications.

Ion-exchange capacity is one of the most fundamental quantities for characterization of any ion-exchange material. For a strong ion-exchanger, the capacity can readily be determined by direct titration. Various types of capacities can be expressed in different manners. The equilibrium ion-exchange capacity for a strong ion-exchanger can be determined by direct titration of strong

cation exchanger (in H^+ form) with a strong base. Majority of the synthetic inorganic ion-exchangers behaves as a weak ion-exchanger and therefore, the direct titration is not reliable. In this case ion-exchange capacity is determined by replacement of hydrogen ions from the exchanger phase by the counter ions of a neutral salt solution and hence determination of the equilibrium ion-exchange capacity is done by pH-titrations. Maximum ion-exchange capacity equal to the number of immogenic groups per specified amount of ion-exchanger may directly be determined by simple column operation passing the electrolytic solution over the ion-exchange material (in H^+ form) and titrating the liberated acid in the effluent by a standard base solution. Although the pure ion-exchange capacity of a solid ion-exchanger can be determined in several ways, a gravimetric method (157) offers for many ion-exchangers the advantage of relatively high accuracy and very simple equipment requirements for only one difference weighing without any analytical chemical determination of ion. Break-through capacity (158) i.e., the useful capacity for utilising the column operations, is of importance when the rate of exchange is slow. This rate may be so slow that the total capacity may not be utilised in an actual operation. The operation is discontinued at break-through before reaching the complete equilibrium. This capacity which is utilized until break-through occurs is known as break-through capacity or dynamic capacity. It depends upon operating conditions and is lower than the equilibrium ion-exchange capacity.

The ion-exchange material must be studied for chemical stability in acidic and basic media to check its limitations.

The distribution of an ion between the exchanger and solution phases is a measurement of selectivity. Often, the ion-exchanger takes up certain ions in preference to the other present counter ions. This selectivity may depend, mainly upon: (i) Donnan potential, (ii) sieve action, and (iii) complex formation. The selectivity is an important factor to study the separations. On the basis of distribution coefficients it is possible to predict the separation of one ion from the other.

The inorganic ion-exchangers have found numerous important analytical applications as categorised below:

(i) Purification of substances on a large scale,
(ii) Separation of one ion from the other on a small ion-exchanger column,
(iii) Ion-exchange paper chromatographic separations,
(iv) Electrophoresis,
(v) Ion-exchanger for gas chromatography,
(vi) Solid state separations,
(vii) Specific spot tests,
(viii) Use of ion-exchanger beads to locate the end point in titration, and
(ix) Use of ion selective electrodes.

Purification on a large scale can be made by passing the sample solution through the ion-exchanger beds which take up certain

materials in preference of others. The exchanger bed can be regenerated into suitable form by conventional methods (139). The technique can also be utilised to recover traces of elements from the dilute solutions. The elements present in ionic form are exchanged by equivalent amount of the counter ion present in the exchanger. The elements can be eluted from the exchanger by suitable electrolytic reagent. Ion-exchange is, with very few exceptions, a reversible process. The metallic ions are exchanged stoichiometrically with hydrogen ions in exchanger phase and the metal ions can be determined indirectly by the application of exchange reactions:

$$nRH^{+} + M^{n+} \rightleftharpoons MR_n + nH^{+}$$

where R represents the structural unit of the ion-exchanger, and H^{+} and M^{n+} are the cations taking part in the ion-exchange. A similar method can be adopted for the replacement of anions by hydroxyl ions stoichiometrically.

Ion-exchange has resolved the most difficult problem in chemical analysis i.e., separation of typical components having similar enough properties. Column chromatography is valuable, since the substances separated are collected quantitatively.

Since the crystalline ion-exchangers have cavities of definite size, they also possess ion sieve properties. The counter ions having larger radii than the holes in the cavity cannot penetrate and therefore, they can be separated from those smaller ions which

can easily enter into the cavity. These separations were first achieved by Clearfield on zirconium phosphate crystals (160) and are summarized below:

Zirconium phosphate and anhydrous metal salt were heated in a platinum dish. The exchange reaction taking place is represented by the following equation:

$$Zr(HPO_4)_2.H_2O + 2/X\ MCl_X \rightleftharpoons Zr(M)_{2/X}(PO_4)_2 + 2HCl + H_2O$$

When zinc chloride or hafnium chloride were exchanged a new phase was obtained which persisted to about 2/3 of total capacity of the exchanger. These wide ranges of metal content forming the same structure indicate that solid solutions of cation within crystal lattice are forming. The fact that a variety of cation type gives the same phases (almost identical interplaner spacing but different intensities) indicates that the crystal lattice remains rigid with the cations occupying similar exchange sites. This is unlike the behaviour of zirconium phosphate exchanging ions in aqueous electrolyte solution where the lattice expands by the movement of the α-zirconium phosphate layers to accommodate hydrated cations. The elution of cations with dilute acid solutions proved the phenomenon as ion-exchange, the cations could also be removed by contacting the exchange phases with gaseous hydrogen chloride.

Some ion-exchange separations were also achieved. A solution containing equal parts of lithium chloride and caesium chloride was

evaporated to dryness and the dry salt mixture was ground together with α-zirconium phosphate. On heating the mixture at 125°C lithium exchanged leaving caesium because the cavities are large enough to permit a cation of about 2-6° A. Thus Cs^+ should be excluded as was observed experimentally.

However, very few literature is available on ion-exchange in molten salt. Alberti and Allulli (161) treated ion-exchange on amorphous zirconium phosphate in molten nitrates. They found that lithium ion is greatly preferred over potassium ions by the exchanger.

Alberti also studied the specific conductance of amorphous zirconium phosphate in Li^+, Na^+, K^+ and Cs^+ forms over the range 2-40% conversions (162). The specific conductance of Li^+ and Cs^+ forms was found to decrease with percent conversion while that of the Na^+ and K^+ forms first increases and then decreases as conversion proceeds. A tentative model was proposed to explain the observed phenomenon.

Spectrophotometry is an important technique for the determination of substances at low level of concentration or at trace analysis level. Spectrophotometry applied in visible region, commonly known as colorimetry, is preferred because of its simplicity and suitability. When a colour is observed by a particular reaction, colorimetric procedures are employed to determine the concentration of one of the reacting substances. Last few decades have seen an extensive developments in this field.

Although colorimetric methods are among the earliest instrumental techniques; but even today they are considered to be one of the top ranking methods because of their overall utility. These methods are based fundamentally on the light absorptive capacity of the coloured materials in the solution form. The development of colour is achieved by certain chemical reactions e.g. by oxidation-reduction, acid-base reaction and complex formation.

Colorimetry was recognized about the year 1850. From 1850 to 1900 there appeared some well known methods mainly for inorganic analysis but the progress was slow. Interest has been developed in 20th century and mainly after 1940 in chemical analysis by the development of colorimetric determination of substances of inorganic and organic origin. The interest grew tremendously because of its demand in routine trace analysis. Studies towards inorganic side have been much exhaustive as compared to the organic sphere. The book "Colorimetric determination of traces of metals" by Sandell (163) has become a classic book in the inorganic field. Snell and Snell (164) have also presented an account of developments in this area. Belts too has given a marvellous contribution for the determination of non-metals (165). The periodical reviews in even years of 'Analytical Chemistry' presents an account of developments in this field from time to time (166,167,168).

For spectrophotometric determinations certain requirements must be fulfilled. The important ones are: selection of an optimum wave length, application of Beer's law, stability of the colour

formed (substance responsible for absorption), sensitivity and selectivity of the method.

The selection of an optimum wave length can be made from the absorption spectrum such that the material of interest absorbs electromagnetic radiation at this wave length to a maximum (or to a greater extent). At such a wave length the absorbance will be affected to a less extent by the interferences provided that the interfering substances do not absorb at this wave length.

Beer's law (or Beer-Lambert's law) relates the absorbance with the concentration. In a general way a straight line is obtained on plotting absorbance against the concentration. The deviation from the straight line may also be observed beyond the range of applicability of Beer's law. However, in certain cases, such calibration curves have also been used for determinations.

The sensitivity tells a minimum amount (or concentration) of a component being determined. The selectivity gives the determination of one component or a group of components in presence of others. The reaction may sometimes be specific to be applicable for the determination of only a single component. Such reactions are of enormous importance in chemical analysis. When a particular reaction is not specific it can be made more selective or sometimes specific by the proper adjustment of the different variables.

The stability of the complexes formed may also be determined by the application of spectrophotometry. Determination of mole ratio between the metal ion and the ligand is frequently used to identify

the complexes formed as a result of chemical interactions. The mole ratio can be ascertained by three different procedures viz. (i) the method of continuous variation attributable to Job, (ii) the mole ratio method introduced by Yoe and Jones, and (iii) the slope ratio method given by Harvey and Manning. The use of the first two is in common practice today.

In quantitative chemical analysis the colorimetric determinations of metal has been proved to be the most useful of all the methods. Relatively less work has been reported on vanadium as compared to the other like elements. Since vanadium is commonly associated with metallurgical and biochemical substances its selective estimation in these substances is considered fairly important in chemical analysis.

The present work was undertaken to synthesize an electron ion-exchanger, zirconium phosphoiodate and to study its properties and its application by electron exchange reactions. Stannic silicate has been prepared as an inorganic ion-exchanger on which a number of ligands have been immobilized to make it selective towards certain metal ions. Zinc silicate has been synthesized and sorption of ligands on it has been studied in the same way as that for stannic silicate. Zinc silicate was found particularly useful for the recovery of Pt(IV) from different metal ions. A new chelate ion-exchanger, stannic diethanolamine, has been synthesized and sorption capacity and applications have been studied on it. A spectrophotometric method has been developed for the quantitative estimation of vanadium by brucine.

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C H A P T E R - II

SYNTHESIS OF ZIRCONIUM PHOSPHOIODATE AND ITS USE AS AN ELECTRON-ION-EXCHANGER

CHAPTER - II

SYNTHESIS OF ZIRCONIUM PHOSPHOIODATE AND ITS USE AS AN ELECTRON-ION-EXCHANGER

The analytical applications of ion exchangers are important and new uses are being actively developed. Oxidation is an important process in modern manufacturing industries. As they are insoluble in the medium of oxidation and reduction, electron exchangers are readily separated from the substances in solution with which they have reacted and thus do not cause the interference which is unavoidable in common redox systems. A survey of literature shows that electron exchangers have not been widely used for redox purposes.

The electron exchanger was first developed by Cassidy (1). It can be stated that two of the fundamental particles, the electron and the proton, can be reversibly exchanged between the exchanger and solution phases. Ion exchange resins have been used as electron exchangers (2-7) and as redox ion exchangers (8-11). New inorganic ion exchangers have also been developed mainly for separation purposes and their analytical importance has been reviewed (12-13). Studies on the application of inorganic ion exchangers to redox reactions, however, are sparse. Zirconium molybdate (14), zirconium metatungstate (15) and few others (16-18) have been studied as electron ion exchangers. The studies on zirconium phosphoiodate as an electron-ion-exchanger are described in this chapter. The

determinations of iron(II), titanium(III), arsenic(III), tin(II) and antimony(III) have been quantitatively achieved by their oxidation using this material as an electron-ion-exchanger.

EXPERIMENTAL

Reagents: Zirconium-oxy-chloride (Fluka), phosphoric acid and potassium iodate (BDH) were used. All other chemicals were of analytical grade.

Apparatus: An electrically temperature controlled SICO shaker and Bausch and Lomb spectronic-20 were used for shaking and spectrophotometric determinations respectively. pH measurements were made with an Elico pH meter.

Synthesis: A number of samples were prepared under a range of conditions given in table 2. Into this, a solution of zirconium oxychloride was added with a constant stirring. White precipitate so obtained was kept standing for 24 hours at room temperature. pH adjustment, if any, was made by adding hydrochloric acid or sodium hydroxide. The precipitate was filtered and washed. The filtered product was then dried at 40°C in a temperature controlled oven. To make the exchanger in Cl^- form, it was kept in 1M HCl for 48 hours. Washed with demineralised water and dried again in an oven at 40°C. To make the exchanger in a particular cationic form, it was kept in a basic solution of the corresponding cation (e.g. in calcium hydroxide for the Ca^{2+} form).

TABLE 2

SYNTHESIS OF ZIRCONIUM PHOSPHOIODATE UNDER DIFFERENT CONDITIONS

Sl. No.	Samples	Molarity of reagents			Mixing volume ratio	pH	Composition
		$ZrOCl_2$	H_3PO_4	KIO_3			
1.	S 1	0.1M	0.1M	0.1M	1:1:1	0.0	3:2:1
2.	S 2	0.1M	0.1M	0.1M	2:1:1	0.0	-
3.	S 3	0.1M	0.1M	0.1M	1:1:1	1.0	-
4.	S 4	0.1M	0.1M	0.1M	1:1:1	2.0	-
5.	S 5	0.1M	0.1M	0.1M	1:1:1	3.0	-

RESULTS

Anion Exchange Capacity: Capacity determinations were done by column operation. One gram of exchanger in chloride form was placed on the glass wool support of the column and 1N sodium nitrate solution was passed through it. The effluent was collected in a beaker keeping the flow rate of elution at 0.5-0.6 ml per minute. The chloride i s thus eluted from the column were determined titrimetrically by Mohr's method (19). The results are given in table 3.

Cation Exchange Capacity: The exchanger converted to Ca^{2+} form by keeping it in a solution of $Ca(OH)_2$ was taken in the column and 1N $NaNO_3$

TABLE 3

ANION AND CATION EXCHANGE CAPACITY OF DIFFERENT SAMPLES

Sl. No.	Sample No.	Anion exchange capacity, m.eq g^{-1}	Cation exchange capacity, m eq g^{-1}
1.	S 1	0.29	0.70
2.	S 2	0.22	0.50
3.	S 3	0.20	0.47
4.	S 4	0.15	0.50
5.	S 5	0.17	0.41

solution was passed through it. Calcium ions collected in the beaker as effluent were determined titrimetrically with 0.1M of ethylene-diaminetetraacetic acid solution. The results are presented in table 3.

Cation Exchange Capacity at Different pH: 0.5 g of exchanger in Na^+ form was taken in a conical flask to which solutions of calcium hydroxide and calcium chloride were added in the ratio given in table 4. Eleven such flasks were taken containing various ratios of the required solutions. The flasks were then shaken in a shaking machine for four hours. The difference in the amount of calcium ions initially present in the solution and that remaining in the solution phase after shaking gave the total amount of metal ions taken up by the exchanger. The results are plotted in figure 1 and presented in table 4.

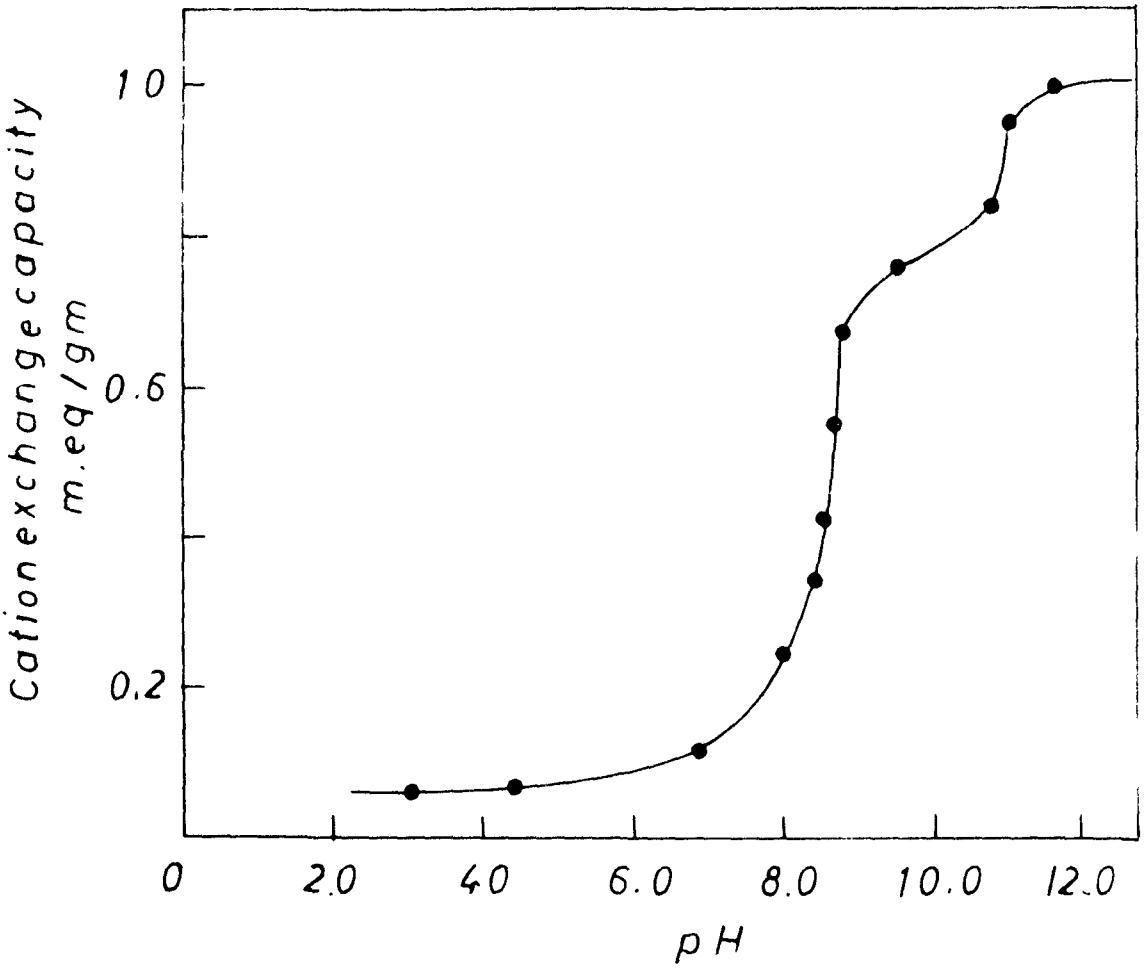

FIG. 1 DEPENDENCE OF ION EXCHANGE CAPACITY ON pH

TABLE 4

CATION EXCHANGE CAPACITY AT DIFFERENT pH

Sl. No.	Calcium hydroxide (0.01N), ml	Calcium chloride (0.01N), ml	Final pH	Capacity, m.eq/g
1.	0	50	3.15	0.05
2.	5	45	4.40	0.06
3.	10	40	6.90	0.11
4.	15	35	8.10	0.24
5.	20	30	8.40	0.33
6.	25	25	8.50	0.42
7.	30	20	8.70	0.54
8.	35	15	8.75	0.66
9.	40	10	9.55	0.75
10.	45	5	10.85	0.84
11.	50	0	11.05	0.94

Anion Exchange Capacity at Different Drying Temperatures: Exchanger in Cl^- form was dried at different temperatures for four hours. Its exchange capacity was determined by taking it in a column and eluted with 1N sodium nitrate solution. Chloride ions collected as effluent was determined by Mohr's method. The results are summarized in table 5.

TABLE 5

ANION EXCHANGE CAPACITY AT DIFFERENT DRYING TEMPERATURES

Sl. No.	Temperature, °C	Anion exchange capacity, m.eq/g
1.	40	0.29
2.	100	0.29
3.	150	0.28
4.	200	0.28

Chemical Stability: To determine the stability of the material, the dissolution of its components in various systems was estimated. 0.5 g of the exchanger in Cl^- form was shaken with 20 ml of solution concerned at 30 ± 1°C for 6 hours. The supernatant liquid was drained off and its phosphate, zirconium and iodate contents were determined. The quantitative determination of phosphate and zirconium were made spectrophotometrically following molybdovanadophosphoric acid method (20) and EDTA titration using xylenol orange indicator method (21) respectively. Iodate was determined iodometrically by standard thiosulphate solution (22). Sample No.1, being chemically more stable, was used for the redox and other studies. The results are summarised in table 6.

TABLE 6

SOLUBILITY OF ZIRCONIUM PHOSPHOIODATE IN DIFFERENT SOLVENTS (mg/50 ml)

Solvents	Sample 1			Sample 2			Sample 3			Sample 4		
	Zirconium in mg	Phosphorus in mg	Iodate in mg	Zirconium in mg	Phosphorus in mg	Iodate in mg	Zirconium in mg	Phosphorus in mg	Iodate in mg	Zirconium in mg	Phosphorus in mg	Iodate in mg
DMF	0.0	0.0	0.000	0.014	0.08	2.44	0.007	0.40	3.1	0.04	0.0	6.5
HNO_3 (1N)	0.004	0.000	0.024	0.0	0.0	4.48	0.0	0.0	16.8	0.0	0.04	4.48
NH_4NO_3 (1N)	0.003	0.06	0.80	0.003	0.0	-	0.04	0.004	13.44	0.0	0.004	5.6
HCl (4N)	0.72	4.0	5.2	0.85	3.52	20.16	0.72	2.96	28.0	0.85	7.6	13.44
HNO_3 (4N)	0.76	8.0	5.12	0.83	2.04	22.4	0.82	11.2	31.2	0.98	6.64	16.8
H_2SO_4 (2N)	0.76	1.6	2.24	0.9	0.64	3.36	0.9	0.4	25.6	0.892	1.04	8.2
HClO (1N)	0.0	6.6	2.24	0.007	0.4	2.8	0.232	4.60	3.2	0.022	3.36	10.4
Methanol	0.0	0.0	1.0	0.0	0.0	0.1	0.0	0.2	0.0	0.0	0.01	-
Acetic acid (4N)	0.0	0.4	1.68	0.07	0.0	-	0.0	0.0	10.4	0.0	-	4.48
Oxalic acid (0.1N)	0.875	9.6	1.56	0.873	3.44	-	0.83	2.24	31.2	0.86	3.12	10.6

Chemical Composition: 300 mg of the powdered material was fused with potassium nitrate and sodium carbonate taken in the ratio 1:3. The fused material was dissolved in water and phosphorus pentoxide present in the dissolved portion was determined gravimetrically by precipitating it as ammonium phosphomolybdate. The collected filtrate contained iodate and its estimation was made iodometrically. The undissolved portion was ignited and weighed as ZrO_2. The results are reported in table 2.

Redox Studies: Oxidations of some oxidisable ions possessing lower redox potentials (28) than Iodate/Iodine have been carried out. The solutions of As(III), Fe(II), Ti(III), Sn(II) and Sb(III) were passed through one gram of the exchanger contained in a glass column of diameter 0.69 cm. The column length was 6 cm. Ti(III) was determined titrimetrically with ferric ammonium sulphate (23). The amount of Ti(III) originally taken minus the amount of Ti(III) found with this method gave the amount of Ti(IV) formed by the exchanger. Since exchanger shows no cation exchange capacity in acidic medium the possibility of retention of metal ions by the exchanger is ruled out. Fe(III) and As(V) were determined titrimetrically with titanous chloride (24) and by the iodometric method (25) respectively. Sn(IV) and Sb(V) were determined by methods reported in literature (26,27). It has been found that titanium(III), iron(II), arsenic(III), tin(II) and antimony(III) are successfully oxidised to Ti(IV), Fe(III), As(V), Sn(IV) and Sb(V) respectively. The results obtained are presented in tables 7, 8, 9, 10 and 11.

TABLE 7

OXIDATION OF IRON(II) TO IRON(III)

Sl. No.	Amount of exchanger (g)	Fe(II) taken (mg)	Fe(III) found (mg)	Standard deviation
1.	1.0	280	265	2.9
2.	1.0	210	195	
3.	1.0	110	120	
4.	1.0	70	60	
5.	1.0	140	130	
6.	1.0	170	165	

TABLE 8

OXIDATION OF ARSENIC(III) TO ARSENIC(V)

Sl. No.	Amount of exchanger (g)	As_2O_5 taken (mg)	As_2O_5 found (mg)
1.	1.0	100	93
2.	1.0	130	134
3.	1.0	120	117
4.	1.0	130	120
5.	1.0	78	78

TABLE 9

OXIDATION OF TITANIUM(III) TO TITANIUM(IV)

Sl. No.	Amount of exchanger (g)	Ti(III) taken (mg)	Ti(IV) found (mg)
1.	1.0	72	71.5
2.	1.0	96	95.0
3.	1.0	115	110.0
4.	1.0	100	98.0

TABLE 10

OXIDATION OF TIN(II) TO TIN(IV)

Sl. No.	Amount of exchanger (g)	Sn(II) taken (mg)	Sn(IV) found (mg)
1.	1.0	70.0	68.0
2.	1.0	120.0	118.5
3.	1.0	168.9	166.9
4.	1.0	220.0	218.0

TABLE 11

OXIDATION OF ANTIMONY(III) TO ANTIMONY(V)

Sl. No.	Amount of exchanger (g)	Sb(III) taken (mg)	Sb(V) found (mg)
1.	1.0	85	83
2.	1.0	90	94
3.	1.0	97	95
4.	1.0	103	103
5.	1.0	110	112

Rate of Oxidation: The rate of oxidation was determined by taking a weighed amount of exchanger in stoppered conical flasks and shaking thoroughly with the solution concerned in a shaking machine. After appropriate intervals of time, the contents of the flasks were filtered and oxidised species formed were determined. The results are presented in table 12 and plotted in figure 2.

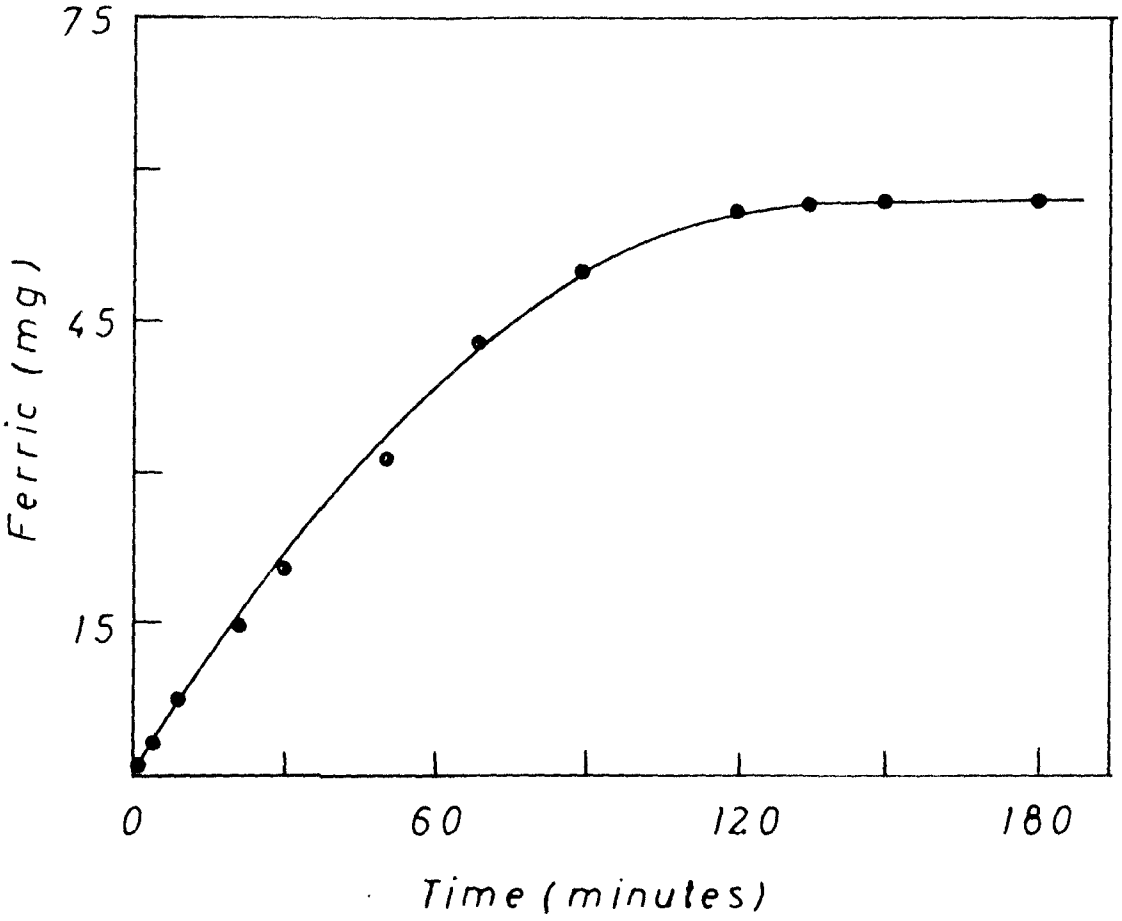

Fig. 2 Rate of oxidation of Fe(II) to Fe(III) by batch process (Fe(II) taken = 60 mg)

TABLE 12

RATE OF OXIDATION OF Fe(II) TO Fe(III)

Amount of Ferrous taken = 60 mg

Time (min.)	Amount of Fe(II) oxidised (mg)
1	9.5
2	15.0
5	25.0
10	35.0
15	39.0
30	49.0
45	51.0
90	51.5
120	51.5

DISCUSSION

The results of ion-exchange capacity summarized in table 3 reveal that zirconium phosphoiodate behaves amphoterically as it possesses anion exchange capacity in acidic medium and cation exchange capacity in basic medium. The anion exchange capacity shows no appreciable variation with change of drying temperature between 40 and 200°C. Therefore, the material may be dried at any temperature in this range. From figure 1 it is evident that cation exchange capacity increases with increase in pH and is maximum at pH 11.

The chemical composition results summarized in table 2 indicate that the molar ratio of Zr:P:I in the exchanger is 2:3:1. The results of table 6 indicate that the compound is stable in neutral medium. High concentrations of acids and bases make the material less stable. However, the material can be used in slightly acidic and slightly basic media without appreciable loss.

The results presented in tables 7 to 11 show that when one gram of the exchanger is taken the method works for low amounts of ions; for higher amounts a larger column must be taken. Thus the column possesses a maximum electron exchange capacity which mainly depends upon its load and column length and is 5 $m.eq.g^{-1}$. When solutions containing higher amount of ferrous ions are passed through one gram of the exchanger only 200 mg is oxidised and rest comes out unoxidised. The electron exchange phenomenon depends on the oxidation potentials of the various redox couples and only those reductants are oxidised

by this exchanger for which the oxidation potential is less than that of the IO_3^-/I_2 redox system. Standard potentials of some of the redox couples are given in table 13. This is further confirmed by Ce(III) which could not be oxidised because the redox potential of the Ce(III)/Ce(IV) couple is higher than that of the IO_3^-/I_2 couple.

TABLE 13

STANDARD POTENTIALS OF SOME REDOX COUPLES

Redox couple	E° volts
$\frac{1}{2}I_2 + 3H_2O = IO_3^- + 6H^+ + 5e^-$	1.195
$Ti^{3+} + H_2O = TiO^{2+} + 2H^+ + e^-$	0.10
$Fe^{2+} = Fe^{3+} + e^-$	0.77
$AsO_2^- + 4OH^- = AsO_3^- + 2H_2O + 2e^-$	-0.67
$Ce^{3+} = Ce^{4+} + e^-$	1.61

The results of figure 2 show that the process of oxidation is slow and takes nearly 2 hours to reach the equilibrium in the batch process. However, in the column operation the slow but continuous flow of liquid disturbs the equilibrium process and the reaction goes favourably for complete conversion of reductant to oxidised product (figure 3).

Zirconium iodate is precipitated when solutions of zirconi oxychloride and potassium iodate are mixed whereas zirconium iodide

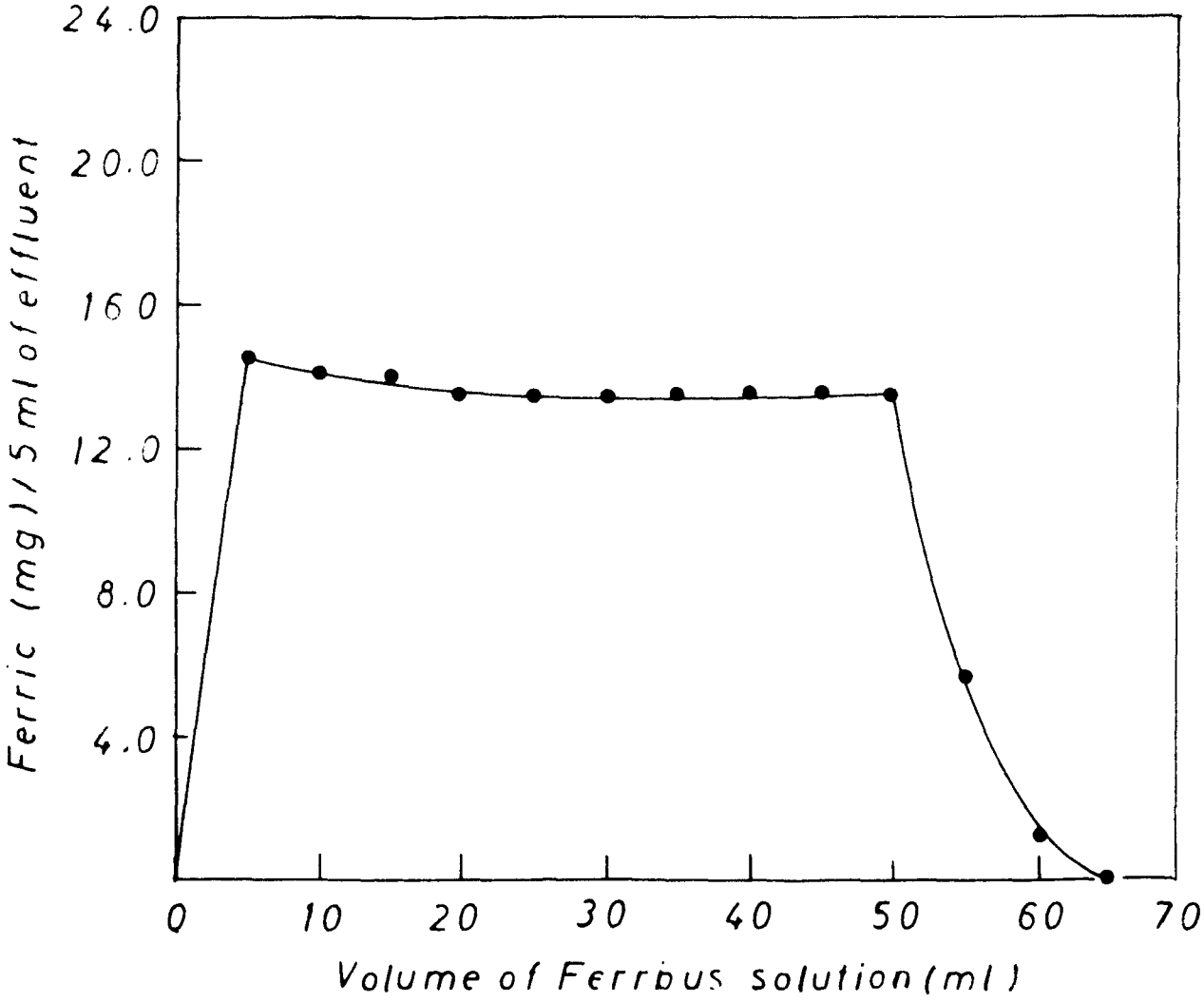

Fig. 3 Conversion of Fe (II) to Fe (III) by column operation

does not precipitate. When synthesis is carried out by the addition of solutions of phosphoric acid and potassium iodate to a solution of zirconium oxychloride, zirconium phosphoiodate is precipitated as a combination of zirconium phosphate and zirconium iodate. Since it is the iodate group, with its IO_3^-/I_2 redox couple, which is responsible for oxidation processes, it is suggested that iodate is bonded at a place which is available for electron exchange. When bonded, the iodate does not change its place but takes part in the electron exchange process according to the following half reaction:

$$IO_3^- + 6H^+ + 5e^- = 3H_2O + \tfrac{1}{2}I_2$$

Iodide is then converted to iodate by air oxidation in the presence of nitric acid. The air oxidation was studied by Berthelot according to the reaction $2KI + 3O_2 = 2KIO_3$ at somewhat elevated temperature. In the present case, the air oxidation also occurs at low temperature since HNO_3 works as a catalyst (29):

$$I_2 + 2HNO_3 + H_2O = 2HIO_3 + 2HNO_2$$

Furthermore, a solid exchanger favours the reaction. Thus zirconium phosphoiodate, when exhausted for oxidation purposes, may be re-oxidized (regenerated by HNO_3). Tables 7-11 show that the results are reproducible.

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CHAPTER - III

SEPARATION AND RECOVERY OF SOME METAL IONS USING PAN SORBED ZINC SILICATE AS CHELATING ION EXCHANGER

CHAPTER - III

SEPARATION AND RECOVERY OF SOME METAL IONS USING PAN SORBED ZINC SILICATE AS CHELATING ION EXCHANGER

There is a revived interest towards the ion exchange properties of silicates (1-4) in recent years and their analytical importance has been demonstrated. The use of chelate ion exchangers is receiving attention during the last few years (5). The selectivity characteristics of chelating resins suggest their utility in several types of separations over the conventional ion exchange resins (6). A number of such ion exchangers have been prepared by the incorporation of ligands on resins (7-9). Because of their high selectivity to certain metal ions the use can be made for chromatographic separations advantageously. Chromatography of metal ions on chelating resin containing a thioglycoloylaxymethyl functional group has been reported (10). However, no such studies have been reported with inorganic exchangers. Zinc silicate was synthesized and it was found that the sorption of PAN (1-(2-pyridyl-azo)-2 naphthol) over it almost alters its properties. The utility of this material has been studied for the selective separations and recovery of certain metals from very dilute solutions.

EXPERIMENTAL

Reagents: Zinc nitrate (BDH), sodium silicate and (1-(2-pyridylazo)-2-naphthol) (BDH) were used. Other chemicals were of reagent grade.

Apparatus: An electric temperature controlled SICO shaker and "Metner Spectra 75" were used for shaking and spectrophotometric measurements respectively. Elico pH meter model Li-10 was used for pH measurements.

Synthesis: A number of samples of zinc silicate were prepared under a range of conditions given in table 14. 0.1M solution of zinc nitrate was mixed with 0.1M solution of sodium silicate in varying ratios. The resulting white precipitate was kept standing for 24 hours at room temperature. pH adjustment, if any, was made by adding hydrochloric acid or sodium hydroxide. The precipitate was filtered, washed and dried at 40°C in a temperature controlled oven. The dried product was kept immersed in a solution of 6M NH_4OH to convert the exchanger into NH_4^+ form. The treatment of exchanger with 6M NH_4OH is important since it increases the stability of the exchanger.

TABLE 14

SYNTHESIS AND PROPERTIES OF ZINC SILICATE

Samples	Conditions of synthesis				Properties	
	Molarity of reagents		Mixing volume ratio	pH	Cation (M^{2+}) exchange capacity m.eq/g	Composition
	Zinc nitrate	Sodium silicate				Moles of Zn : SiO_2
1	0.1	0.1	1:1	0.0	2.35	1:1.25
2	0.1	0.1	2:1	0.0	2.25	-
3	0.1	0.1	1:1	1.0	0.95	-
4	0.1	0.1	1:1	2.0	0.65	-
5	0.1	0.1	1:1	3.0	0.58	-

RESULTS

Cation Exchange Capacity: The ion exchange capacity for H^+ ion was determined by taking the exchanger in H^+ form and then eluting with 1N solution of ammonium acetate. Metal ion capacity was determined by taking M^{2+} with the exchanger and eluting with 1N solution of ammonium acetate. Eluted metal ions were titrated with a solution of ethylenediamine tetraacetic acid. The results are summarized in table 15.

TABLE 15

EXCHANGE CAPACITY OF ZINC SILICATE

Sl. No.	Eluted ion	Exchange capacity, m.eq/g
1.	H^+	0.05
2.	Ca^{2+}	2.38
3.	Cu^{2+}	2.56
4.	Zn^{2+}	2.36
5.	Mg^{2+}	2.33
6.	Fe^{3+}	2.29

Chemical Stability: 200 mg of the exchanger was shaken with 20 ml of the appropriate solvent for 6 hours at room temperature. Zinc released into the supernate was determined titrimetrically with ethylenediaminetetraacetic acid and silicon content was determined spectrophotometrically by molybdenum blue method (11). Results are given in table 16. The results of the stability of sample 1 only are reported here. The values in the table refer to the amounts of Zn and Si dissolved in 20 ml solvent.

TABLE 16

SOLUBILITY OF ZINC SILICATE IN DIFFERENT SOLVENTS

Amount of exchanger taken = 200 mg

Sl. No.	Solvents	Zinc (mg)	Silicon (mg)
1.	Demineralised water	0.0	0.0
2.	Ammonium hydroxide, 6.5N	1.8	0.0
3.	Methanol	0.0	0.0
4.	Nitric acid, 2N	16.25	24.0
5.	Hydrochloric acid, 2N	48.75	13.9
6.	Sulphuric acid, 2N	40.00	48.9
7.	Ammonium acetate, 1N	0.0	0.0
8.	Oxalic acid, 1N	0.81	0.0
9.	Acetic acid, 1N	16.28	15.48
10.	Sodium nitrate, 1N	0.0	0.0

Chemical Composition: A 200 mg portion of the exchanger was heated in a 30 ml of aqua regia for nearly half an hour. This resulted in the dissociation of zinc ions from the silicates. Zinc ions thus released into the supernatant liquid were filtered and quantitatively estimated by titration with ethylenediaminetetraacetic acid. The residue was ignited and weighed as SiO_2. The results are given in

table 14. These results give an apparent ratio of Zn:Si of 1:1.25.

Heat Treatment: Exchanger was dried at different temperatures in a muffle furnace for four hours. Cation exchange capacity of one gram of each of the dried product was determined as described earlier on page 60. The results are presented in table 17.

TABLE 17

CATION EXCHANGE CAPACITY AT DIFFERENT TEMPERATURES

Sl. No.	Temperature, °C	Cation exchange capacity, m.eq/g
1.	40°	2.30
2.	100°	1.70
3.	200°	1.30
4.	300°	0.94
5.	400°	0.26

Chelating Properties: The fact that zinc silicate keeps a firm hold on the sorbed substances has been advantageously used to make it act like a chelating exchanger. The exchanger was kept immersed in an alcoholic solution of PAN for 24 hours to allow complete sorption of the latter. Washed first with alcohol and then with deionized water and dried at 40°C. The yellow coloured zinc-silicate-PAN product so obtained was then used for the separations and recovery of some of

the metal ions. Alcohol and dilute solution of ammonium hydroxide do not cause release of PAN from the exchanger.

Distribution studies: Distribution coefficients of seven metal ions were determined by batch process on PAN-sorbed zinc silicate.

$$Kd = \frac{\text{Amount of metal ion in exchanger phase } g^{-1}}{\text{Amount of metal ion in solution phase } ml^{-1}}$$

The amount of exchanger was 0.5 g and total volume of equilibrating solution was maintained at 25 ml. Shaking was done for six hours. Au(III) (12), Pt(IV) (13) and Ag(I) (14) were determined by spectrophotometric methods, whereas Co^{2+}, Cu^{2+}, Ni^{2+} and Fe^{3+} were estimated volumetrically by EDTA. The Kd values of these ions were determined in deionised water and in solutions of different concentrations of ammonia. The results are presented in table 18.

TABLE 18

Kd VALUES OF METAL IONS

Cations	Kd values, ml g^{-1}						
	*DMW	NH_4OH 1M	NH_4OH 2M	NH_4OH 3M	NH_4OH 4M	NH_4OH 5M	NH_4OH 6M
Cu^{2+}	260.0	147.5	50.8	14.52	8.72	1.0	0.0
Ni^{2+}	280.0	18.0	9.8	2.60	0.0	0.0	0.0
Co^{2+}	560.0	110.0	72.0	45.70	45.7	45.7	45.7
Fe^{3+}	360.0	40.0	17.1	0.0	0.0	0.0	0.0
Pt^{4+}	0.9	0.8	0.8	0.8	0.9	0.9	0.9
	*DMW	NH_4OH 0.001M	NH_4OH 0.005M	NH_4OH 0.01M	NH_4OH 0.05M	NH_4OH 0.1M	NH_4OH 0.5M
Ag^{+}	840	480	220	176	104	72	0.60
Au^{3+}	600	780	195	154	98	52	0.48

*DMW = Demineralised water

Column Separations: A glass column (length 43 cm, i.d. 0.39 cm^2) was filled to a height of 10 cm with two grams of the exchanger fully sorbed with PAN. The column was washed with 50 bed volumes of

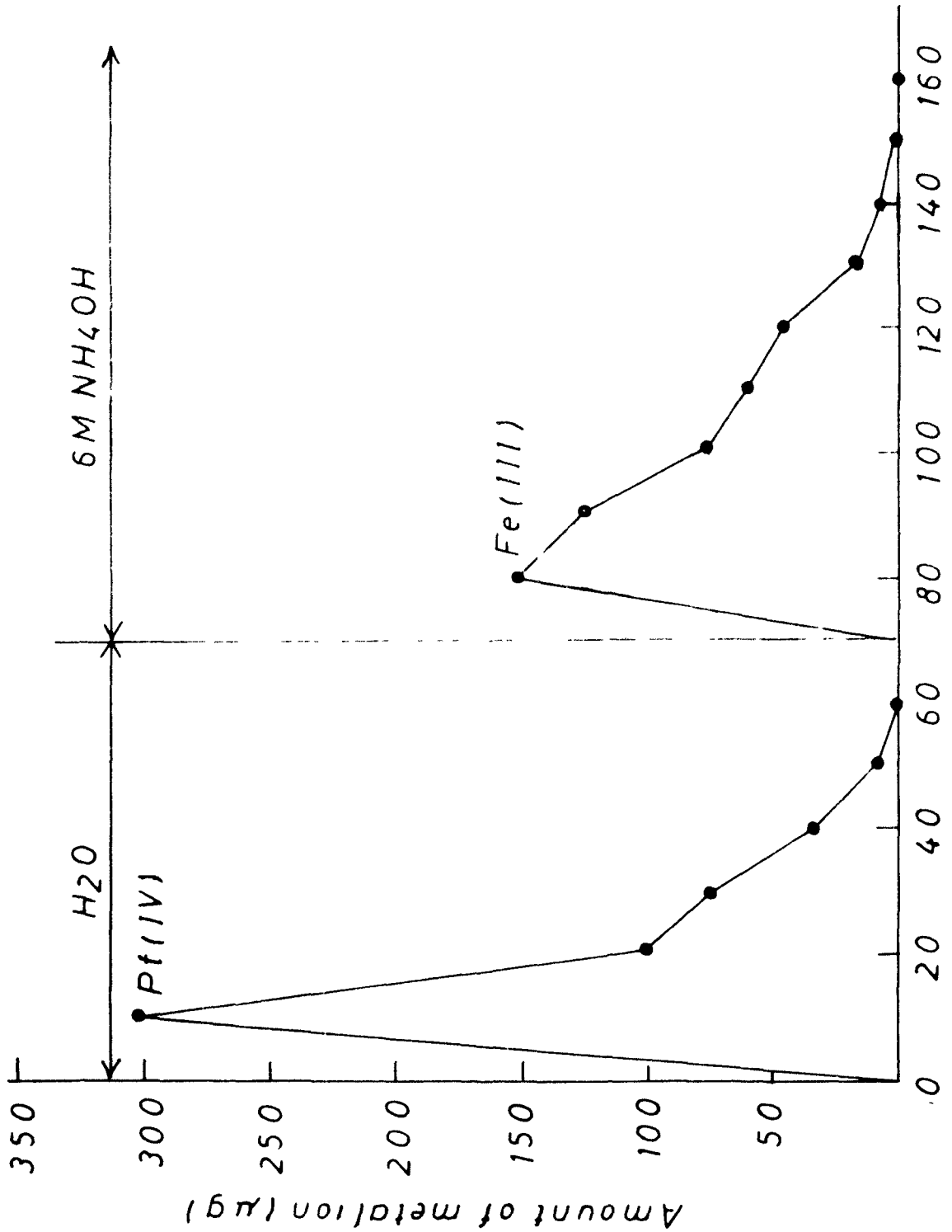

Fig.4 Separation of Pt(IV) – Fe (III)

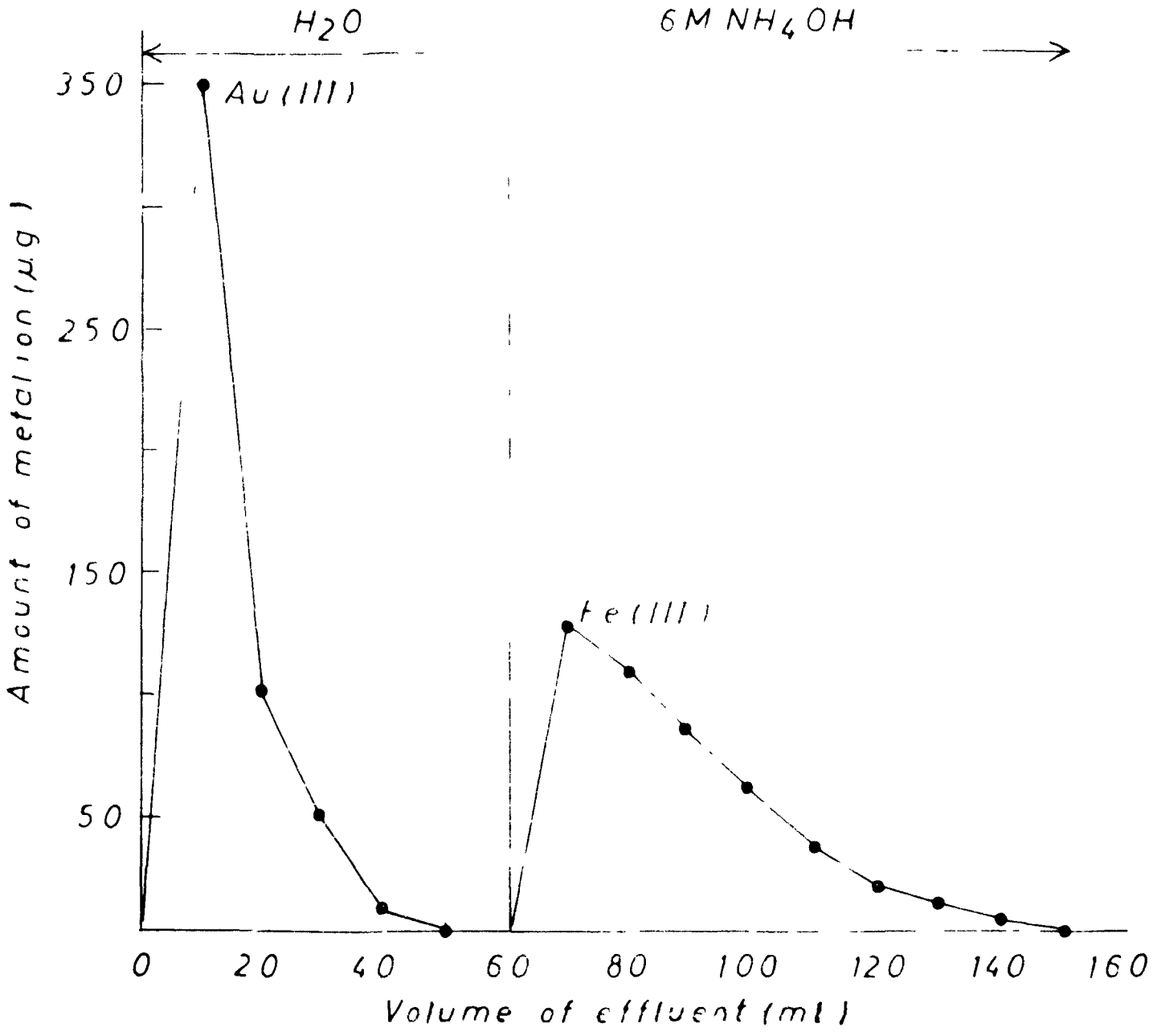

Fig 5 Separation on Au(III) - Fe(III)

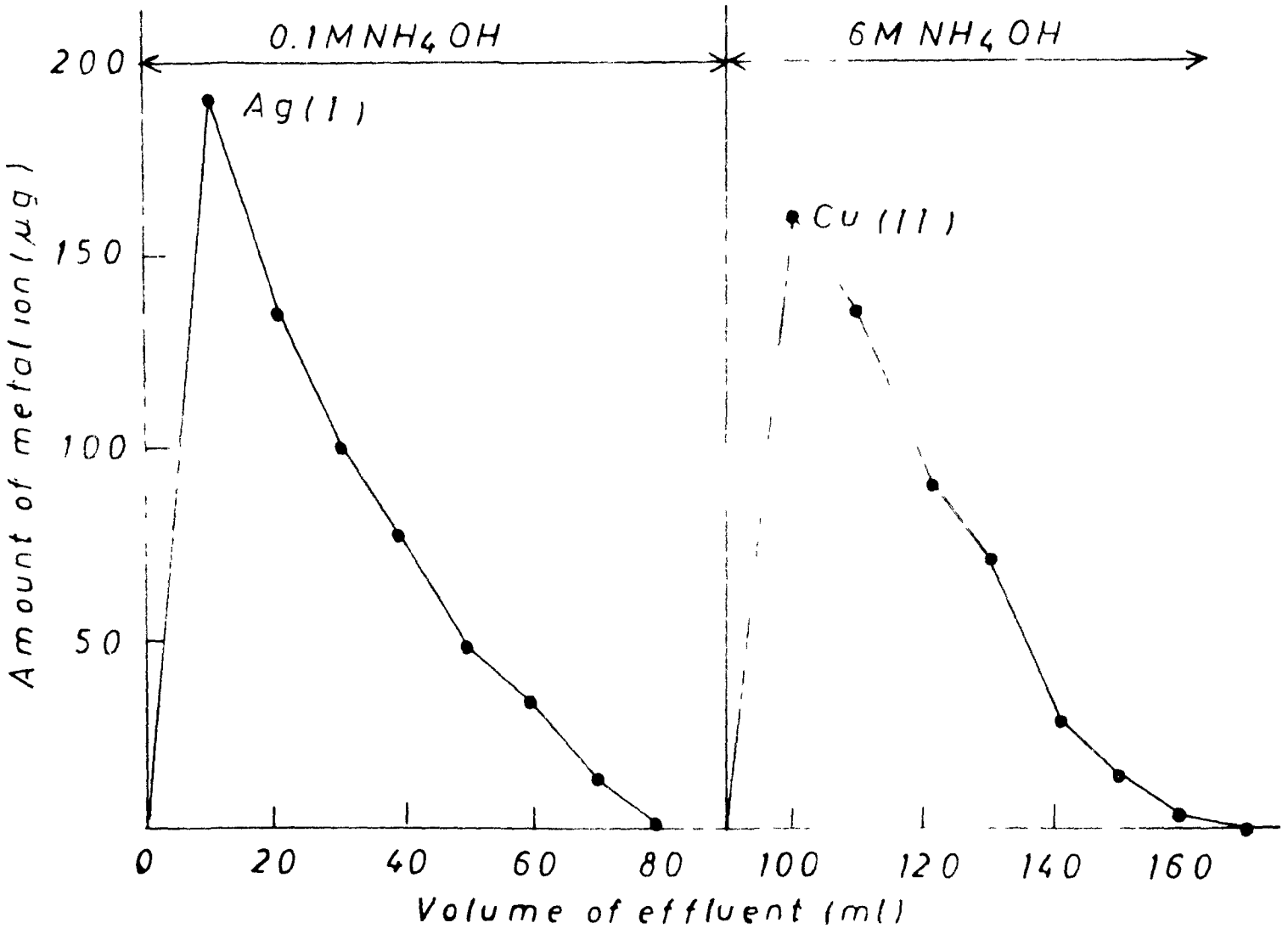

Fig. 6 Separation of Ag(I) - Cu(II)

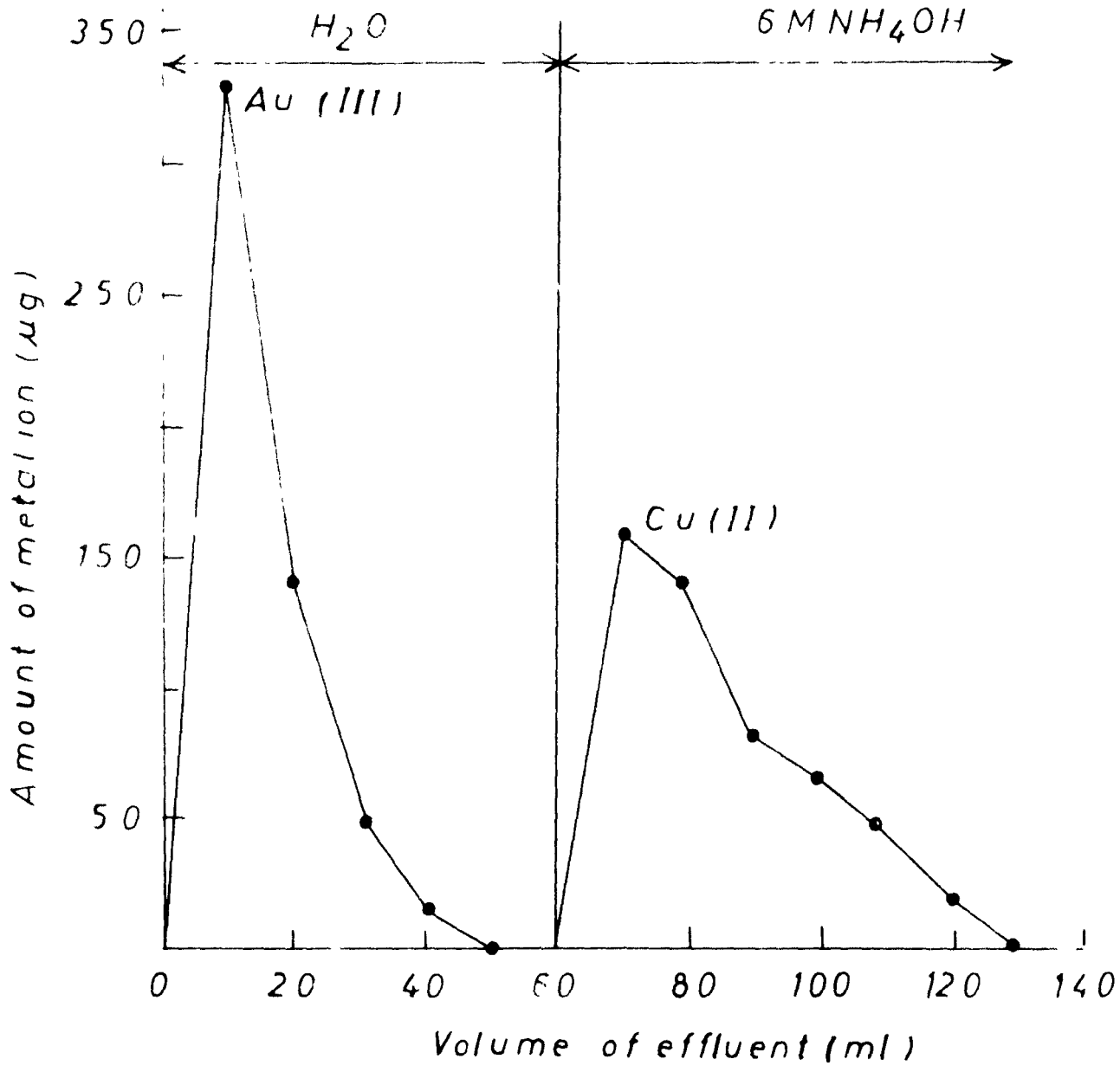

Fig. 7 Separation of Au (III) – Cu (II)

demineralised water and 10 bed volumes of buffer of pH 3.6. The sample solutions containing the metal ions desired to be separated was passed onto the column at a flow rate of 1 to 2 ml min^{-1}. Table 19 shows a list of separations successfully achieved on a column of PAN sorbed zinc silicate. The order of separation and the eluents used are presented in figures 4, 5, 6 and 7.

TABLE 19

SEPARATIONS ON ZINC-SILICATE-PAN COLUMNS

	Mixture	Eluent	Eluate (ml)	Amount loaded	Amount found	% Error
1a	Pt(IV)	DMW	50	500 µg	493 µg	1.40
	Fe(III)	NH_4OH,6M	100	40 mg	40.25 mg	0.65
1b	Pt(IV)	DMW	50	500 µg	515 µg	3.00
	Fe(III)	NH_4OH,6M	80	500 µg	490.35 µg	1.93
1c	Pt(IV)	DMW	60	10 mg	9.20 mg	7.80
	Fe(III)	NH_4OH,6M	100	1 mg	1.03 mg	3.00
2	Au(III)	DMW	40	500 µg	510 µg	2.00
	Fe(III)	NH_4OH,6M	80	500 µg	510.12 µg	2.04
3a	Ag(I)	NH_4OH,0.1M	80	13.8 mg	14.0 mg	1.5%
	Cu(II)	NH_4OH,6M	70	5.8 mg	6.0 mg	3.4%
3b	Ag(I)	NH_4OH,0.1M	90	1.38 mg	1.42 mg	2.80
	Cu(II)	NH_4OH,6M	80	600 µg	615 µg	2.50

(TABLE 19 CONTINUED)

	Mixture	Eluent	Eluate (ml)	Amount loaded	Amount found	% Error
3c	Ag(I)	NH_4OH, 0.1N	90	600 µg	608 µg	1.30
	Cu(II)	NH_4OH, 6N	70	600 µg	610 µg	1.66
4a	Au(III)	IMW	40	475 µg	470 µg	1.05
	Cu(II)	NH_4OH, 6N	70	4.1 mg	4.0 mg	2.46
4b	Au(III)	IMW	30	1.0 mg	1.02 mg	2.00
	Cu(II)	NH_4OH, 6N	100	1.14 mg	1.09 mg	4.38

Recovery of Pt(IV) and Au(III): Solutions of Pt(IV) and Au(III) containing five fold excess of iron, cobalt, copper and nickel were passed through 2 grams of the exchanger. Unsorbed Pt(IV)/Au(III) was collected as effluent and determined quantitatively by spectrophotometric method. The retained metal ions, Co^{2+}, Cu^{2+}, Ni^{2+} and Fe^{3+} were eluted out with 6N NH_4OH. The results are summarized in table 20.

TABLE 20

RECOVERY OF Pt(IV) AND Au(III) IONS AT pH 3.6 FROM SOLUTIONS CONTAINING 5 mg EACH OF Co(II), Ni(II), Cu(II) AND Fe(III)

Ions measured	Initial amount of ion taken (mg)	Amount of ion eluted (mg)	Recovery %
Pt(IV)	1.0	0.99	99
Pt(IV)	5.0	4.80	96
Au(III)	1.0	0.99	99
Au(III)	5.0	5.06	101

DISCUSSION

The results of synthesis and properties of zinc silicate presented in table 14 together with the chemical stability results given in table 16 show that sample 1 is chemically more suitable than any of the other samples. Therefore, this product was chosen for detailed study.

From the results given in table 15 it can be inferred that zinc silicate works as an extremely weak cation exchanger and hence desisted any release of hydrogen ions. It is, therefore, desirable that the exchanger should not be allowed to make contact with any solution that contains high concentration of hydrogen ions. The metal ions capacity, however, is sufficiently high and varies from 2.29 to 2.36 m.eq/g. The results presented in table 17 shows a loss in capacity at higher temperatures.

The results of the stability of zinc silicate presented in table 16 show that zinc silicate can be used in nearly neutral media, water, salt solutions, alcohols, dilute acids and ammonia concentrat upto 6M without an appreciable loss. High concentration of acid, however, affects the exchanger and causes dissociation of its constituents to some extent. Dilute acids, too, are detrimental since they render the exchanger unusable. Even a prolonged contact with a concentrated solution of sodium chloride failed to dislodge the hydrogen ions from the exchanger phase—in the presence of which complexing agents are not at all sorbed by the exchanger.

Most remarkable property of zinc silicate is its ability to

sorb complexing agents. The exchanger which so far had an almost equal affinity for most of the metal ions becomes selective to certain metal ions and discriminatory to some. This is reflected from the results presented in table 21 which indicate that while untreated zinc silicate has a sorption capacity between 2.29 to 2.36 m.eq.gm^{-1}, treated zinc silicate has sorption capacity of 0.0 to 0.8 m.moles gm^{-1}. The reduced sorption capacity is indicative of the fact that sorbed metal ions no more occupy the pores or room that was available with the untreated exchanger. Instead, sorption capacity now depends on the number of sites available for the chelation.

TABLE 21

SORPTION CAPACITY OF SOME METAL IONS ON TREATED AND UNTREATED ZINC SILICATE

Sl. No.	Metal ions	Sorption capacity of untreated exchanger, m.moles g^{-1}	Sorption capacity of treated exchanger, m.moles g^{-1}
1.	Cu^{2+}	2.36	0.80
2.	Ni^{2+}	2.40	0.76
3.	Ag^{+}	2.00	0.05
4.	Pt^{4+}	2.44	0.10
5.	Au^{3+}	2.30	0.00
6.	Fe^{3+}	2.29	0.70

The results presented in tables 18 and 21 indicate that zinc-PAN-silicate shows a selective sorption for Co(II), Cu(II), Fe(III) and Ni(II) whereas desorption for Ag(I), Pt(IV) and Au(III) ions. This paved the way for the easy separations of the two class of ions. The reason for selective sorption and desorption of certain types of metal ions can be attributed to the larger difference in the stability constants of the metal-PAN complexes. The elution is based on the stability constant of the metal-eluting ligand. Metal-eluting ligand having high stability constant will be eluted first.

List of separations presented in table 19 are based on the observation that unlike Fe(III), Ni(II), Cu(II) and Co(II) which were retained by the exchanger, Ag(I), Au(III) and Pt(IV) passed out unsorbed. This led to the successful separation of Fe(III) from Pt(IV), Fe(III) from Au(III), Cu(II) from Ag(I) and Cu(II) from Au(III).

Table 20 shows the successful recoveries of Pt(IV) and Au(III) from solutions containing iron(III), copper(II), nickel(II) and cobalt(II). In the presence of five fold excess of these metal ions, neither of them could be detected in the water eluate containing platinum and gold. The retained metal ions, Co(II), Cu(II), Ni(II) and Fe(III), were easily eluted out with 6M NH_4OH. This shows the importance of PAN-sorbed zinc silicate in the recovery of precious metal ions.

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CHAPTER - IV

METAL ION CHELATION CHROMATOGRAPHY ON COMPLEXONES SORBED STANNIC SILICATE

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METAL ION CHELATION CHROMATOGRAPHY ON COMPLEXONES SORBED STANNIC SILICATE

INTRODUCTION

The selectivity of ion-exchange resins for metal ions can be increased by a suitable choice of the complexing agent. As a result they can be used as an analytical tool for separation purposes where theoretical principles can be applied and selective separations can be achieved. Use has been made of complexones for the preparation of new chelating resins for separating metal ions on the basis of complex formation (1-6). Inorganic ion exchangers can be used likewise. Sorption of 8-hydroxyquinoline on Permsil separates ions such as Co-Ni, Cd-Pb-Zn at trace levels (7). When complexing agents are immobilised on the exchanger, it prefers one (or a few) metal ion species much more strongly than any other according to its complexing ability. Thus zinc silicate sorbed with PAN, (1-(2-pyridylazo-2-naphthol), has been used to separate Fe(III)-Pt(IV), Fe(III)-Au(III), Cu(II)-Ag(I) and Cu(II)-Au(III) (8). The present work summarizes the possibility of using xylenol orange, eriochrome black T and 1,10-phenanthroline as complexing agents for the separation of metal ions on strongly adsorptive stannic silicate exchanger. The aim was to establish conditions for the separation of a number of metal ions on columns of this material.

EXPERIMENTAL

Reagents and solutions: Stannic chloride pentahydrate (Poland) and sodium silicate (Merck) were used. All other chemicals were of AnalaR grade.

Solutions of Eriochrome black T, xylenol orange and 1-10 phenanthroline were prepared in distilled ethanol. 0.01M solutions of Cu(II), Cd(II), Ni(II), Th(IV), Fe(III) and alkaline earth metals were prepared in demineralised water. Hg(II) solution was prepared by dissolving $Hg(NO_3)_2$ in 0.1N HNO_3.

Apparatus: A temperature controlled SICO shaker and an Elico pH meter model LI-10 were employed for shaking and pH measurements respectively.

Synthesis: Stannic silicate was prepared by mixing 0.1M solutions of stannic chloride pentahydrate and a 0.1M solution of sodium silicate (9). The white precipitate formed was kept standing at room temperature for over 24 hours. The precipitate was filtered and dried at 40°C. The dried product so obtained was kept immersed in solutions of desired complexone for 48 hours. It was then washed first with demineralised water and then with ethanol. Washing was continued to remove excess complexone. The washed product was then dried at 40°C and used for batch process and column operations.

RESULTS

Sorption Capacity: The sorption capacity of the exchanger was determined by batch process. 0.5 g exchanger was shaken with a solution of 0.02N of the desired metal ion in a conical flask containing 25 ml of a solution of pH 6. After being shaken for 6 hours at room temperature the mixture was decanted and the amount of metal ion remaining in the filtrate was determined by chelometric titrations. The sorption capacity of some metal ions are reported in table 22.

TABLE 22

SORPTION CAPACITY OF COMPLEXONES SORBED STANNIC SILICATE FOR VARIOUS METAL IONS

Name of complexing agent sorbed	Colour of the exchanger	Sorption capacity in m.moles g^{-1}					
		Fe(II)	Fe(III)	Cu(II)	Mn(II)	Th(IV)	Mg(II)
Xylenol Orange	Yellow	0.38	0.38	0.60	0.00	0.62	0.00
Eriochrome black T	Violet	0.00	-	-	0.38	0.00	0.38
1,10 phenanthroline	White	0.60	0.00	-	-	-	-

Rate of Sorption: The rate of sorption of Th(IV) and Cu(II) was determined by a batch process. A fixed concentration (0.6 m.moles) of metal ions in a solution of pH 6 was shaken with xylenol orange sorbed stannic silicate at different intervals of time and the amount of unsorbed ion was determined in the eluate. The sorbed amount of metal ion was then calculated by the difference in the amount initially taken and the amount found after shaking. The results are plotted in figure 8 and presented in table 23.

TABLE 23

RATE OF SORPTION OF Th(IV) AND Cu(II) AT pH 6

Time (min.)	Th(IV) sorbed, (m.moles)	Cu(II) sorbed, (m.moles)
0.0	0.00	0.00
0.5	0.08	0.08
1.0	0.18	0.18
2.0	0.26	0.25
3.0	0.30	0.28
5.0	0.34	0.30
10.0	0.34	0.30
15.0	0.34	0.30
20.0	0.34	0.30

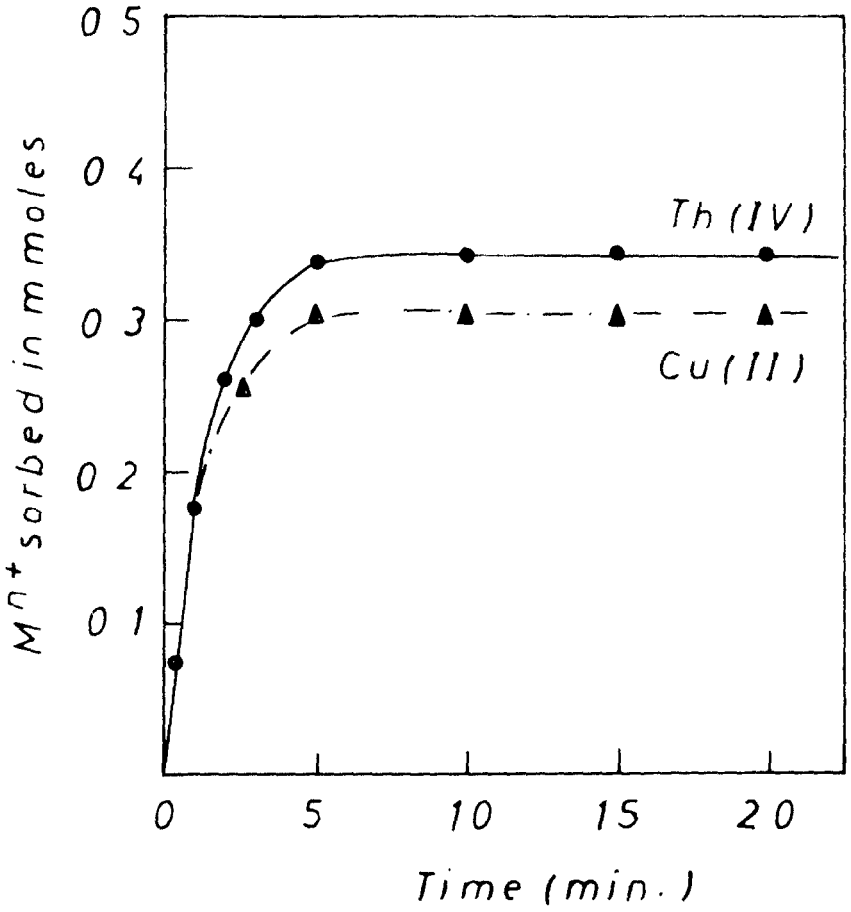

Fig. 8 Rate of sorption of Cu (II) & Th (IV)

Comparison with Silica Gel: Under similar conditions sorption of all the three complexing agents on silica gel was studied. It was observed that extremely poor adsorption of complexing agent occurs on silica gel. This observation is pointer to the reason why stannic silicate functions much better than silica gel.

pH range: The pH range within which the exchanger can be safely used was determined by shaking with solutions of different pH for 6 hours. Results show that bleeding of complexones occurred in solutions where pH was less than 1 and more than 8.

Distribution Coefficients of Metal Ions at Different pH

(i) **Xylenol orange sorbed stannic silicate:** To a stoppered conical flask containing 24 ml solutions of different pH (1 to 6) and 1 ml of 0.01M metal ion solution was added. The mixture was equilibrated with 200 mg exchanger for 4 hours. The amount of unsorbed metal ion was then determined in the solution mixture. The distribution coefficient, Kd, is given by:

$$Kd = \frac{\text{Amount of metal ion in exchanger phase } g^{-1}}{\text{Amount of metal ion in solution phase } ml^{-1}}$$

The results of variation of Kd with pH for different metal ions are plotted in figure 9 and presented in table 24.

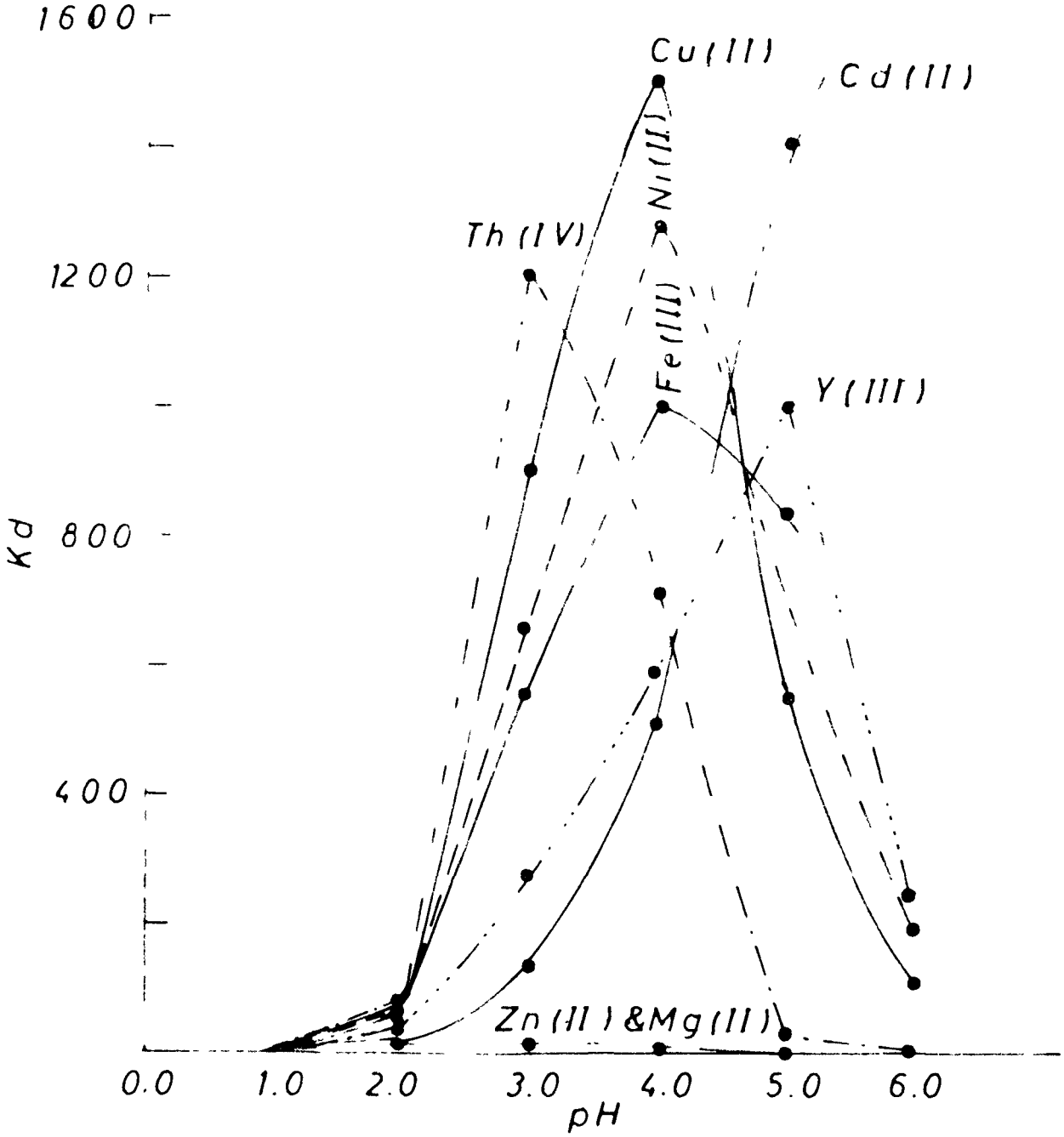

Fig 9 Kd values of some metal ions at different pH

TABLE 24

Kd VALUES OF SOME METAL IONS ON STANNIC SILICATE SORBED WITH XYLENOL ORANGE

Metal ions	Kd					
	pH 1	pH 2	pH 3	pH 4	pH 5	pH 6
Cu(II)	3.00	48	900	1300	580	120
Ni(II)	0.0	90	910	1280	720	210
Mg(II)	0.0	6	-	-	-	-
Zn(II)	0.0	8	15	8	-	-
Y(III)	4.0	17	280	590	1000	270
Th(IV)	12.0	71	1200	710	8	2
Fe(III)	0.0	90	533	1000	840	-
Cd(II)	0.0	2	132	500	1400	-

(ii) Eriochrome black T sorbed stannic silicate: Kd values were determined in the same way as that for the xylenol orange sorbed exchanger. The results are given in table 25.

TABLE 25

Kd VALUES OF METAL IONS ON STANNIC SILICATE SORBED WITH ERIOCHROME BLACK T

Metal ions	Kd									
	pH 1	pH 2	pH 3	pH 4	pH 5	pH 6	pH 7	pH 8	pH 9	pH 10
Ca(II)	0.0	52.5	300.0	43.5	1168	T.A.	T.A.	T.A.	T.A.	T.A.
Mg(II)	0.0	50.0	65.0	200.0	375	1075	T.A.	T.A.	T.A.	T.A.
Zn(II)	2.5	16.2	42.1	375.0	1150	T.A.	T.A.	T.A.	T.A.	T.A.
Ba(II)	8.0	275.0	375.0	510.0	1125	T.A.	T.A.	T.A.	T.A.	T.A.
Sr(II)	0.0	24.7	31.2	37.5	210	300	T.A.	T.A.	T.A.	T.A.
Cu(II)	0.0	1.4	1.2	1.2	0.0	0.0	0.0	0.0	0.0	0.0
Ni(II)	1.2	1.2	1.6	1.4	1.0	0.0	0.0	0.0	0.0	0.0

T.A. = Total adsorption

Separations: On the basis of difference in Kd values separations were tried on a 30 x 0.39 cm^2 glass column. 2.0 g exchanger was taken on a glass wool support of the column. Solutions of metal ions to be separated were then passed through the column at a flow rate of 0.5 ml min^{-1}.

(i) Separations on xylenol orange sorbed stannic silicate: Successful separations of four sets of metal ions, Cu-Zn, Cu-Cd, Th-Zn and Th-Cd have been achieved on a column containing stannic silicate sorbed with xylenol orange. Zn(II) was eluted with 0.5M NaCl and a mixture of

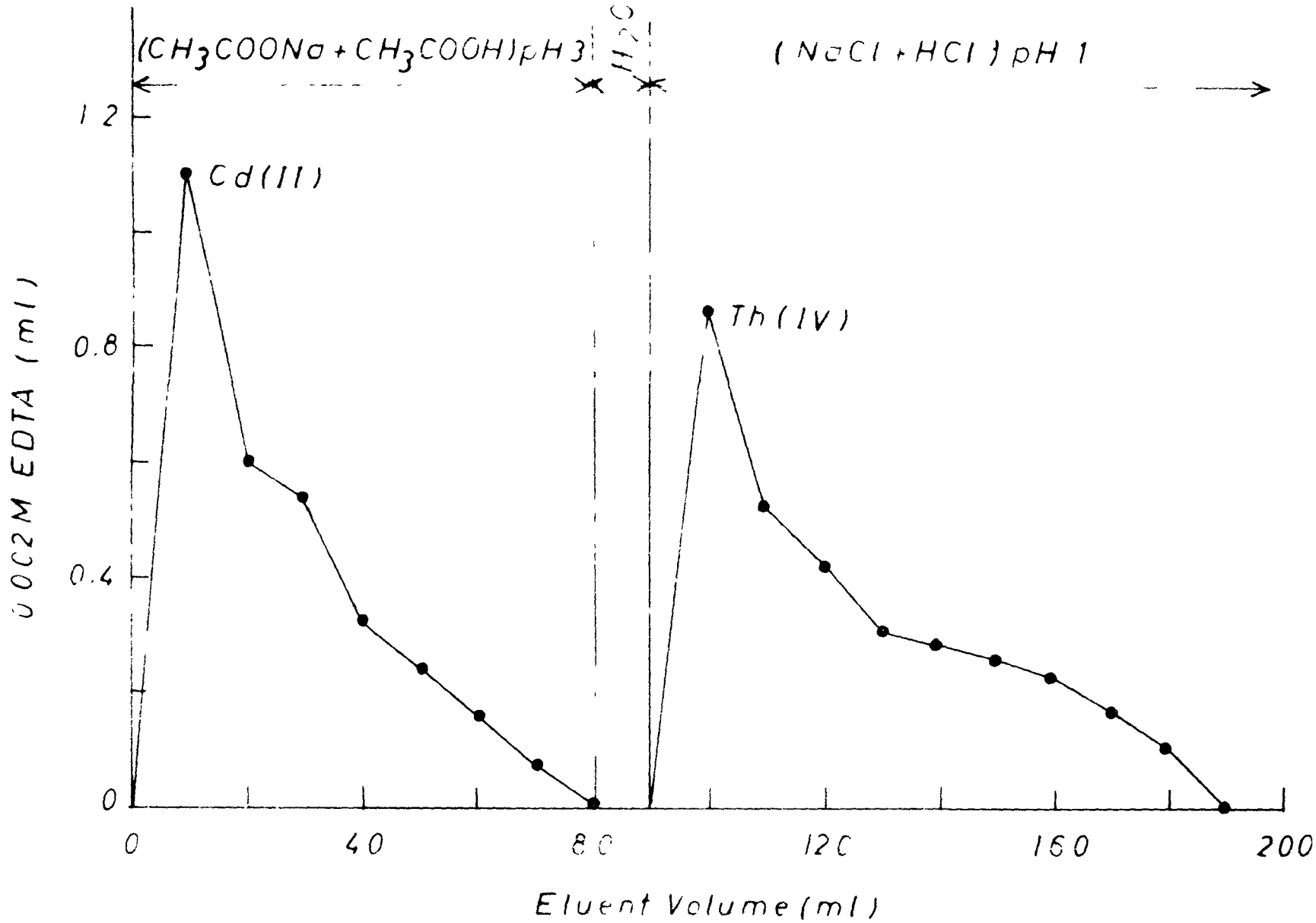

Fig. 10 Separation of Cd (II) - Th (IV)

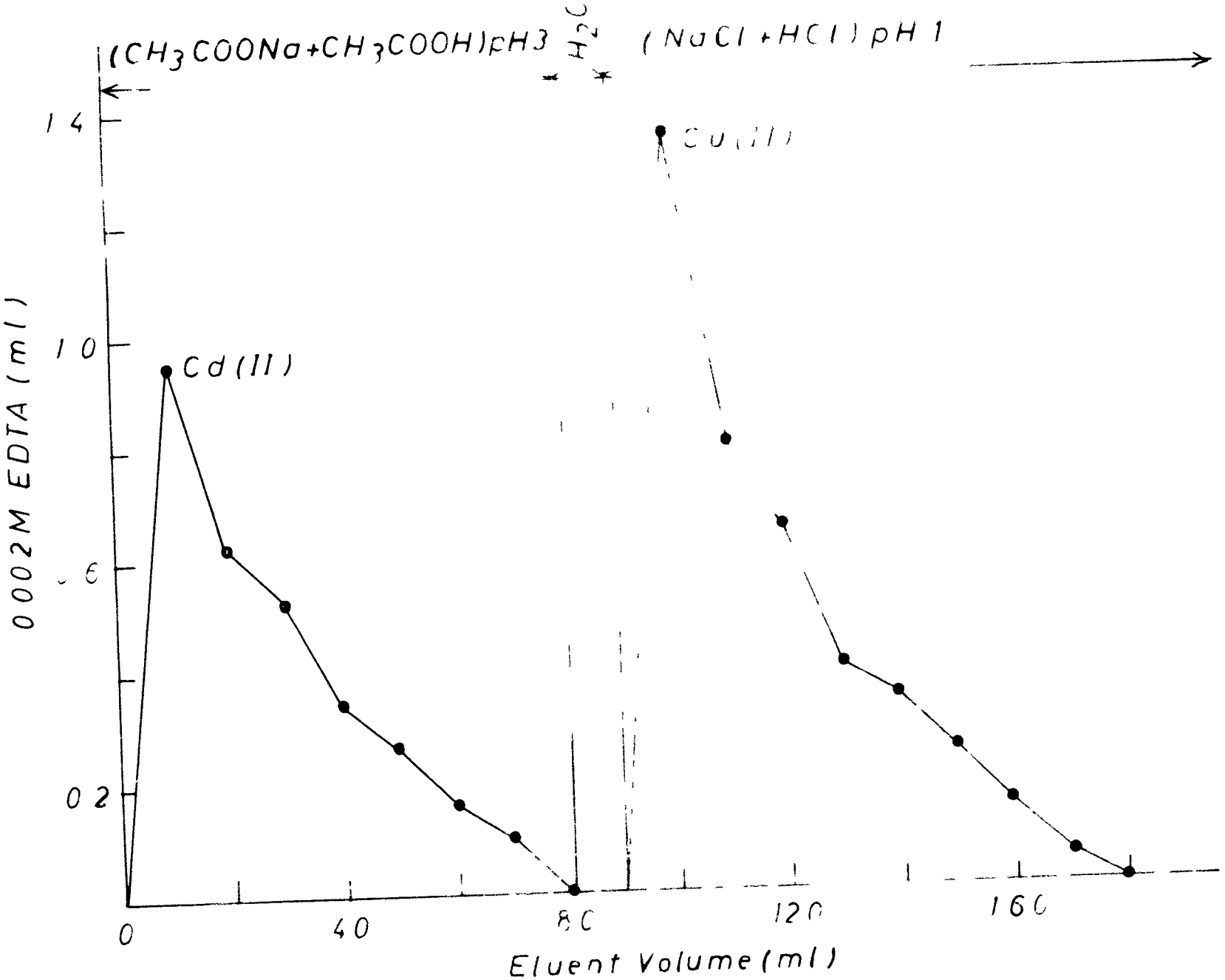

Fig. 11 Separation of Cd(II) – Cu(II)

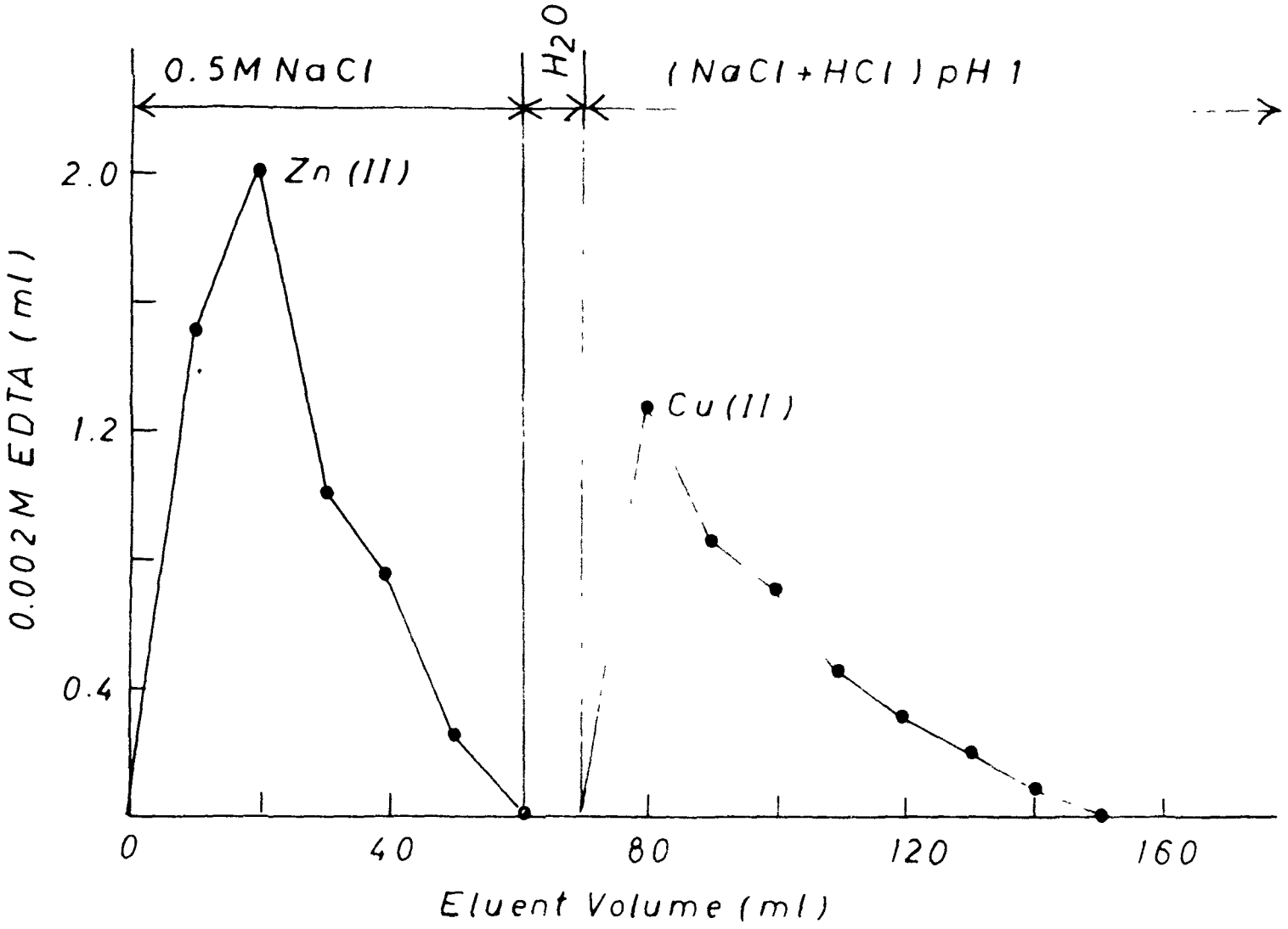

Fig 12 Separation of Zn (II) – Cu (II)

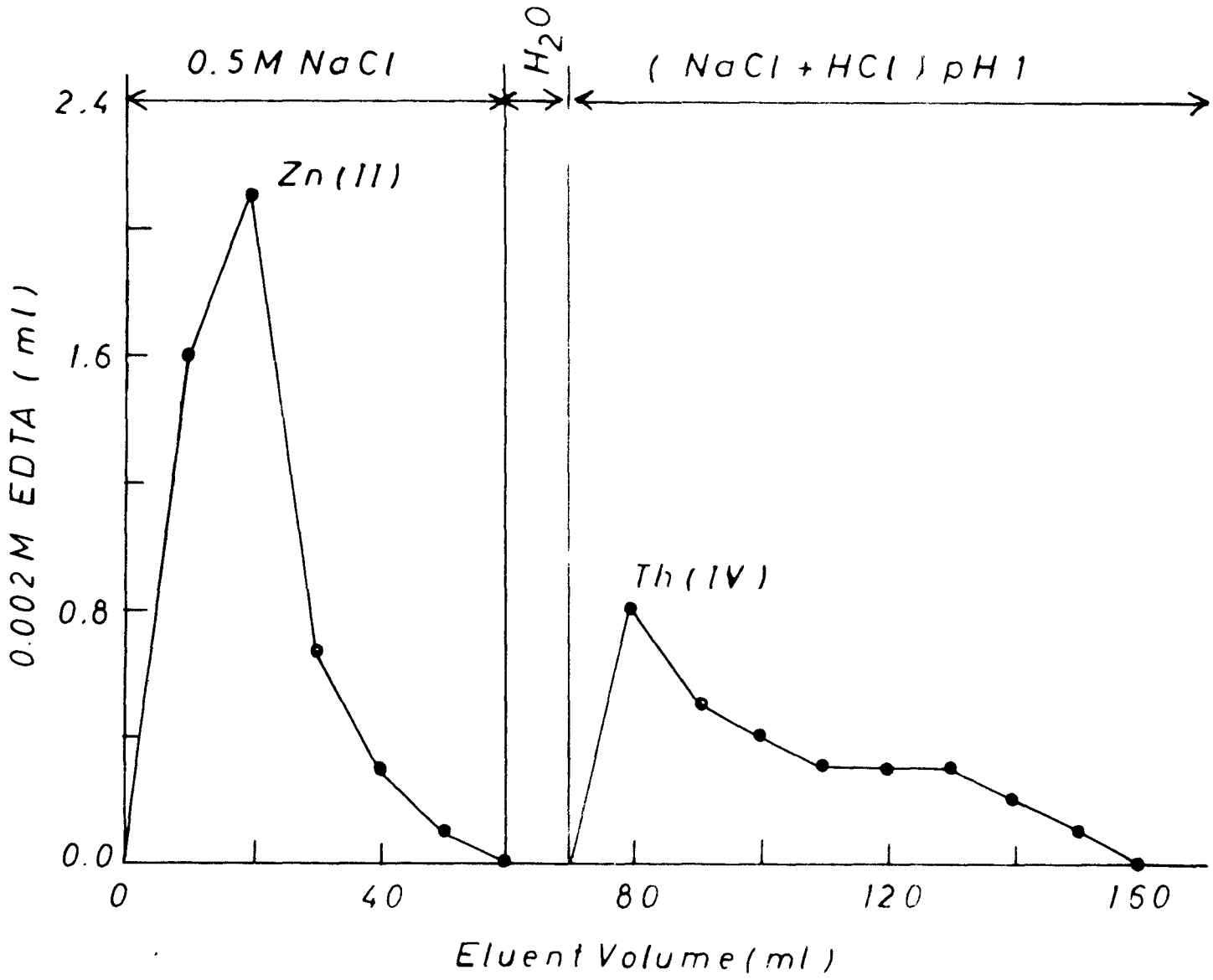

Fig. 13 Separation of Zn (II) – Th (IV)

(CH_3COONa + CH_3COOH) adjusted to pH 3 was used for the elution of Cd(II). Elution of Th(IV) and Cu(II) was made by a mixture of 0.1M NaCl and 0.1M HCl adjusted to pH 1. The results are presented in figures 10, 11, 12 and 13 and in table 26.

TABLE 26

SEPARATIONS ON STANNIC SILICATE XYLENOL ORANGE COLUMN

Sl. No.	Mixture	Eluent	Eluate (ml)	Amount loaded, (µg)	Amount found, (µg)	% Error
1.	Cu(II)	(HCl + NaCl) pH 1	80	485	480	1.03
	Zn(II)	NaCl, 0.5M	50	510	505	1.37
2.	Cu(II)	(HCl + NaCl) pH 1	80	485	485	0.68
	Cd(II)	(CH_3COOH + CH_3COONa) pH 3	70	500	490	2.00
3.	Th(IV)	(HCl + NaCl) pH 1	90	568	569	0.80
	Cd(II)	(CH_3COOH + CH_3COONa) pH 3	70	500	493	1.42
4.	Th(IV)	(HCl + NaCl) pH 1	90	568	570	0.55
	Zn(II)	0.5M NaCl	70	510	508	0.59

(ii) <u>Separations on 1,10-phenanthroline sorbed stannic silicate:</u> Remarkable separations of iron(II) from iron(III) have been achieved on stannic silicate sorbed with 1,10-phenanthroline. Fe(III) was

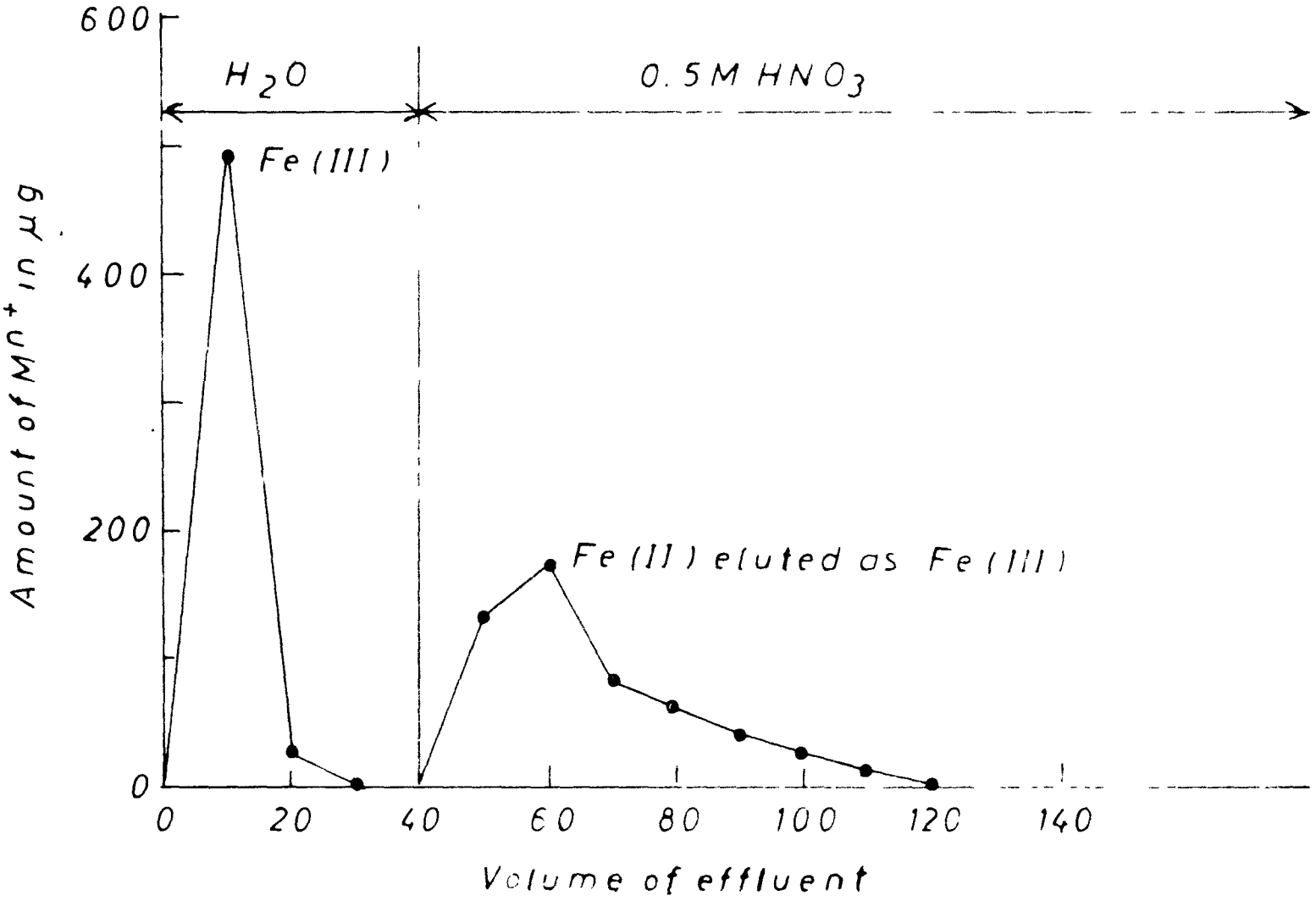

Fig. 14 Separation of Fe (II) from Fe (III)

selectively retained by the exchanger. The results are summarised in table 27 and presented in figure 14.

TABLE 27

SEPARATIONS ON 1,10-PHENANTHROLINE SORBED STANNIC SILICATE COLUMNS

Sl. No.	Mixture	Eluent	Elute (ml)	Amount loaded, (µg)	Amount found, (µg)	% Error
1.	Fe(III)	Demineralised water	20	500	495	1.00
	Fe(II)	HNO_3, 0.5M	90	525	521	0.72
2.	Fe(III)	Demineralised water	20	1000	998	0.20
	Fe(II)	HNO_3, 0.5M	90	525	522	0.60

DISCUSSION

Stannic silicate which originally had the hydrogen ion-exchange capacity of 0.5 m.eq.g^{-1} lost its hydrogen ion-exchange capacity after treatment with the complexones but gained the sorption capacity. This sorptive ability of the treated stannic silicate shows that adherence of the complexing agents to the exchanger offers sites for the chelation of metal ions. Sorption of complexing agents like xylenol orange, eriochrome black T and 1,10-phenanthroline were successfully achieved. Stannic silicate which is colourless originally acquired the colour of the sorbed complexone or complex formed by the action of metal ions with the complexone alone. The movement of the complex thus formed can be observed visually in the column.

The results of the sorption capacity determinations (table 22) show that complexones sorbed stannic silicate has a sorption capacity between 0.5 to 0.6 m.moles g^{-1} for different metal ions. In these studies it was observed that xylenol orange sorbed stannic silicate does not take up alkaline earth metal ions whereas stannic silicate sorbed with eriochrome black T exclusively retained alkaline earths. Application of 1,10-phenanthroline to stannic silicate made it selective to Fe(II) ions and immune to Fe(III) ions. These results inferred that the metal ions forming stable complexes with complexones are preferred by the solid phase and this forms the basis of selectivity. Furthermore, changing the complexones open a way to prepare the ion exchanger in desired form for the particular problem of separation.

The results of table 23 and figure 8 show the rate of sorption of metal ions on xylenol orange sorbed stannic silicate wherefrom it can be seen that maximum sorption of both Th(IV) and Cu(II) is attained in 5 min. This fast equilibration rate is one of the desirable properties of chelating exchangers (10) and an advantage over the general ion-exchangers. Other desirable properties such as high capacity for metals of interest, high selectivity and high mechanical strength or toughness of the exchanger are adequate with complexones sorbed on stannic silicate. The sorption capacity for metal ions is due to the presence of complexing agents whereas high selectivity depends upon the stability constant of the metal chelating group. The presence of all the four qualities of a chelating ion-exchanger in this case constitutes its advantage over the organic chelating exchangers wherein high capacity and toughness are the two competitive factors.

It can be seen from figure 9 that distribution of metal ion between exchanger phase and solution phase depends upon the pH of the equilibrating solution. Stannic silicate sorbed with xylenol orange shows different affinity for number of metal ions viz. Cu(II), Th(IV), Cd(II), Y(III), Ni(II), Fe(III) and Mg(II). Among these metal ions, the values at pH 5.0 gives the maximum difference in Kd values. This difference in Kd values is probably due to the difference in stabilities of complexes formed. This made possible the separation of two class of metal ions - those sorbed appreciably at pH 5 from those sorbed to a lesser degree at pH 5. The separations practically achieved on this principle are: Th(IV) from Cd(II) and Cu(II) from

Cd(II) (Figs.10 and 11). Metal ions like Zn(II) and Mg(II) are not at all sorbed. This is because sorbed complexing agent, xylenol orange, does not form stable complexes with Zn(II) and Mg(II). Separation of Zn(II) from Cu(II) and Th(IV) is based on this principle.(Figs.12 and 13).

Determination of Kd values of alkaline earth metal ions on eriochrome black T further confirms the inference that application of a complexing agent makes the exchanger 'choosy'. Eriochrome black T sorbed stannic silicate sorbs only alkaline earths and does not take up metal ions that do not form stable complexes with eriochrome black T. Hence alkaline earth metals as a group might be separated from other metal ions.

The results summarized in table 27 show some separations of Fe(II) from Fe(III) ions on the columns of stannic silicate sorbed with 1,10 phenanthroline. Since Fe(II) forms a stable complex with 1,10 phenanthroline it is selectively retained whereas Fe(III) comes out unretained. Fairly stable Fe(II) - 1,10 phenanthroline complex did not allow elution of Fe(II) as such. Conversion of Fe(II) to Fe(III) with HNO_3, causes the detachment of iron from the complexone. This separation gives an important application as the same metal in different valence states behaves in a different manner. Other separations based on this principle may also be tried.

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CHAPTER - V

STANNIC DIETHANOLAMINE AS A NEW CHELATING ION EXCHANGER

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STANNIC DIETHANOLAMINE AS A NEW CHELATING ION EXCHANGER

The chelate ion exchangers have received attention recently. The preparation and properties of chelating resins and their utility in separation science are described viz. polystyrene based oxime (1,2), o-hydroxypropiophenone oxime-divinylbenzenestyrene resin (3), thioglycolate-chelating resin (4), carboxylate type (5) chelating exchanger Dowex-A1, N-acylphenyl hydroxylamines (6). Many other specific resins have also been reported. In the complexing tendency the material behaves similar to the complexing agent and the metal ion can be detached from the column leaving the complexing agent. However, possibility has not been explored towards inorganic chelate ion exchangers. Therefore it was decided to prepare a new inorganic chelate ion exchanger, stannicdiethanolamine and to study its properties and applications.

EXPERIMENTAL

Reagents and solutions: Stannic chloride pentahydrate (Poland) and diethanolamine (BDH) were used. Other chemicals used were of AnalaR grade.

0.01M solutions of Cu(II), Cd(II), Ni(II), Th(IV) and Fe(III) were prepared in demineralised water. Hg(II) and Pb(II) solutions were prepared by dissolving their nitrates in 0.1N HNO_3. For Pt(IV) solution, platinic chloride was dissolved in 0.1M HCl.

Apparatus: A temperature controlled SICO shaker was used for shaking. ELICO pH meter model Li-10 and Metzer Spectra 75 were used for pH and spectrophotometric measurements respectively.

Synthesis: 0.1M solution of stannic chloride was mixed with 0.4M solution of diethanolamine in different ratios as given in table 28. The mixture was kept standing for 24 hours at room temperature to ensure complete precipitation. The white precipitate so obtained was filtered and dried at 60°C in an oven. The dried product was washed with demineralised water. It is vitally important that exchanger should not be allowed to come in contact with water while it is hot. The hot product, if kept in water, shows a strong hydrolysis. Therefore, after being dried in the oven, the exchanger was kept at room temperature till it cooled down completely. The exchanger was now washed with water and was redried at 40°C in the oven.

TABLE 20

CONDITIONS OF PREPARATION AND PROPERTIES OF STANNICDIETHANOLAMINE

Samples	Conditions of synthesis			Properties		
	Molarity of Reagents		Mixing volume ratio	Nature of precipitation	Sorption capacity in m.moles per gm	Ion-exchange capacity
	Stannic chloride	Diethanolamine				
S1	0.1M	0.1M	1:1	No precipitation	-	-
S2	0.1M	0.4M	1:2	No precipitation	-	-
S3	0.1M	0.4M	2:1	A thick precipitate	0.55	0.0
S4	0.1M	0.4M	4:1	Mild precipitation	-	-
S5	0.1M	0.4M	1:2	No precipitation	-	-

RESULTS

Sorption Capacity: The sorption capacity of the exchanger was determined by a batch process. 0.5 g of the exchanger was shaken with 1 ml solution of known concentration of desired metal ion in a conical flask containing 24 ml of sodium borate-boric acid buffer (pH 6). After being shaken for six hours at room temperature the mixture was decanted and the amount of metal ion remaining in the filtrate was determined by chelometric titration. Sorption capacity of stannic-diethanolamine for different metal ions was calculated and the results are summarised in table 29.

TABLE 29

SORPTION CAPACITY FOR DIFFERENT METAL IONS

Sl. No.	Metal ion	Sorption capacity in m.moles/g
1.	Cu(II)	0.55
2.	Ni(II)	0.50
3.	Fe(III)	0.45
4.	Zn(II)	0.55

Stability: 0.5 g of the exchanger was shaken in a conical flask for four hours in solutions in which its dissolution was to be checked. The supernate was decanted and Sn(IV) was determined spectrophoto-

metrically with phenylfluorone (7). Diethanolamine was determined colorimetrically by pyrocatechol method (8). Solubility of the exchanger was checked in water, different concentrations of hydrochloric acid, ammonium hydroxide, sodium hydroxide and nitric acid. The results are summarised in table 30.

TABLE 30

SOLUBILITY OF STANNICDIETHANOLAMINE

Solvent	Solubility in (mg/50 ml)	
	Sn(IV)	Diethanolamine
Distilled water	0.00	0.00
HCl, 0.1M	0.05	0.06
HCl, 0.5M	0.10	0.20
HCl, 1M	0.21	0.28
HCl, 2M	0.34	0.40
NH_4OH, 1M	0.00	0.00
NH_4OH, 2M	0.15	-
NH_4OH, 4M	0.40	-
NaOH, 1M	24.00	-
HNO_3, 2M	0.90	14.00

Composition: To determine tin, 500 mg of the exchanger was dissolved in 100 ml of concentrated HCl in a conical flask. The volume was made upto 250 ml with distilled water and the solution was heated for an hour in an atmosphere of CO_2. It was then cooled and tin in its reduced state was titrated against 0.1N potassium dichromate solution (9). Diphenylamine was used as an indicator.

For the determination of diethanolamine, another 500 mg of the exchanger was taken in a round bottom flask and 100 ml of 10N NaOH was added dropwise. The apparatus assembly is shown in figure 14. The amine distilled into the 1% solution of boric acid was determined by titration with 0.1N HCl to a bromocresol green end point (10).

The results of the analysis of sample 3 are as follows:

Amount of exchanger taken	=	1.000 g
Amine obtained after distillation	=	0.5690 g
	=	5.42 m.moles
Amount of tin(IV) found	=	0.2890 g
	=	2.44 m.moles
Molar ratio of Sn:Diethanolamine	=	(1:2.221)

I.R.Spectrum: I.R.spectrum of the sample S3 was obtained by using KBr disc. The spectrum is shown in figure 15.

Sorption of Metal Ions at Different pH: To a glass stoppered conical flask containing 200 mg of the dry exchanger and 20 ml of 0.2M hydrochloric acid - 0.2M sodium acetate solutions (adjusted to pH 1-7), 1 ml of 0.1N metal ion solution was added. The mixture was then

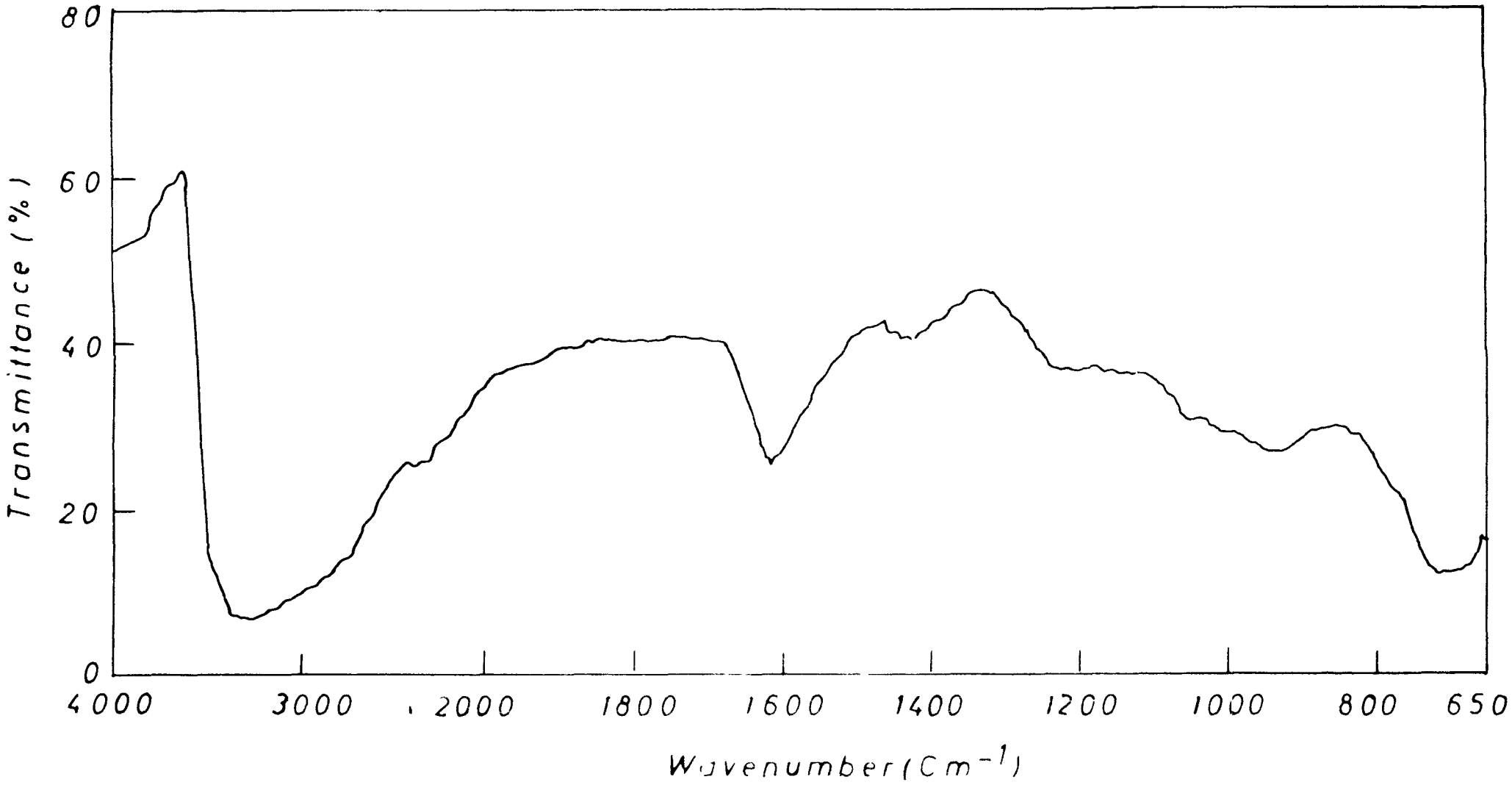


Fig 15 IR Spectrum of Stannic diethanolamine

shaken for 6 hours at room temperature. The supernate was drained off and the amount of metal ion remaining in it was determined by chelometric titrations. The results showing variation in sorptive ability of the metal ions in solutions of different pH are presented in table 31 and figure 16.

TABLE 31

SORPTION OF METAL IONS AT DIFFERENT pH

Metal ions	Amount of metal ion sorbed in m.moles					
	pH 1	pH 2	pH 3	pH 4	pH 5	pH 6
Cu(II)	0.0×10^{-2}	0.60×10^{-2}	1.2×10^{-2}	1.4×10^{-2}	1.6×10^{-2}	1.68×10^{-2}
Hg(II)	0.6×10^{-2}	1.68×10^{-2}	1.72×10^{-2}	1.76×10^{-2}	1.76×10^{-2}	1.76×10^{-2}
Pb(II)	1.40×10^{-2}	1.50×10^{-2}	1.54×10^{-2}	1.60×10^{-2}	1.62×10^{-2}	1.66×10^{-2}
Cd(II)	1.62×10^{-2}	1.08×10^{-2}	1.14×10^{-2}	1.26×10^{-2}	1.44×10^{-2}	1.62×10^{-2}
Zn(II)	0.4×10^{-2}	1.0×10^{-2}	1.1×10^{-2}	1.48×10^{-2}	1.08×10^{-2}	0.6×10^{-2}
Fe(III)	0.0×10^{-2}	0.0×10^{-2}	0.8×10^{-2}	1.2×10^{-2}	1.26×10^{-2}	1.44×10^{-2}
Ni(II)	0.0×10^{-2}	0.10×10^{-2}	0.70×10^{-2}	1.26×10^{-2}	2.00×10^{-2}	2.04×10^{-2}
Mn(II)	0.0×10^{-2}	0.0×10^{-2}	0.20×10^{-2}	0.64×10^{-2}	1.56×10^{-2}	1.60×10^{-2}

Break through Capacity: The break through capacity was determined by column operation. Solutions of copper nitrate containing

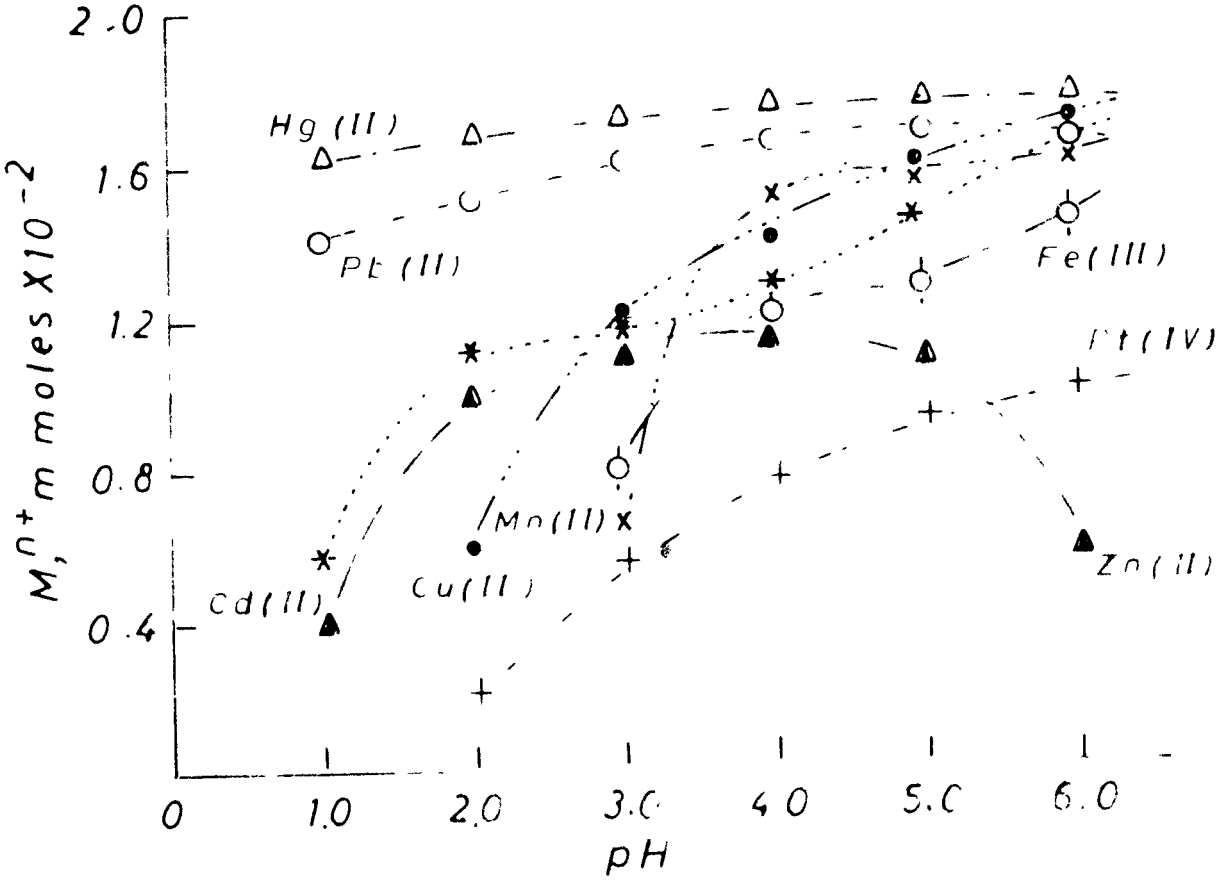


Fig. 16 Sorption of metal ions at different pH

0.57 mg/10 ml, 0.38 mg/10 ml and 0.192 mg/10 ml of Cu(II) were passed through a column loaded with 2 g of stannicdiethanolamine on its glass wool support. The flow rate was adjusted to 0.5 ml min^{-1}. The amount of Cu(II) in each fraction collected as effluent was determined. The results are summarized in tables 32, 33 and 34 and plotted in figure 17.

TABLE 32

BREAK THROUGH CAPACITY OF STANNICDIETHANOLAMINE

Concentration of feed solution = 0.576 mg/10 ml

pH of the solution = 6.0

Flow rate = 0.5 ml min^{-1}

Fractions	Cu(II) in effluent, (µg)
10	0.038
20	0.139
30	0.267
40	0.374
50	0.515
60	0.515
70	0.515

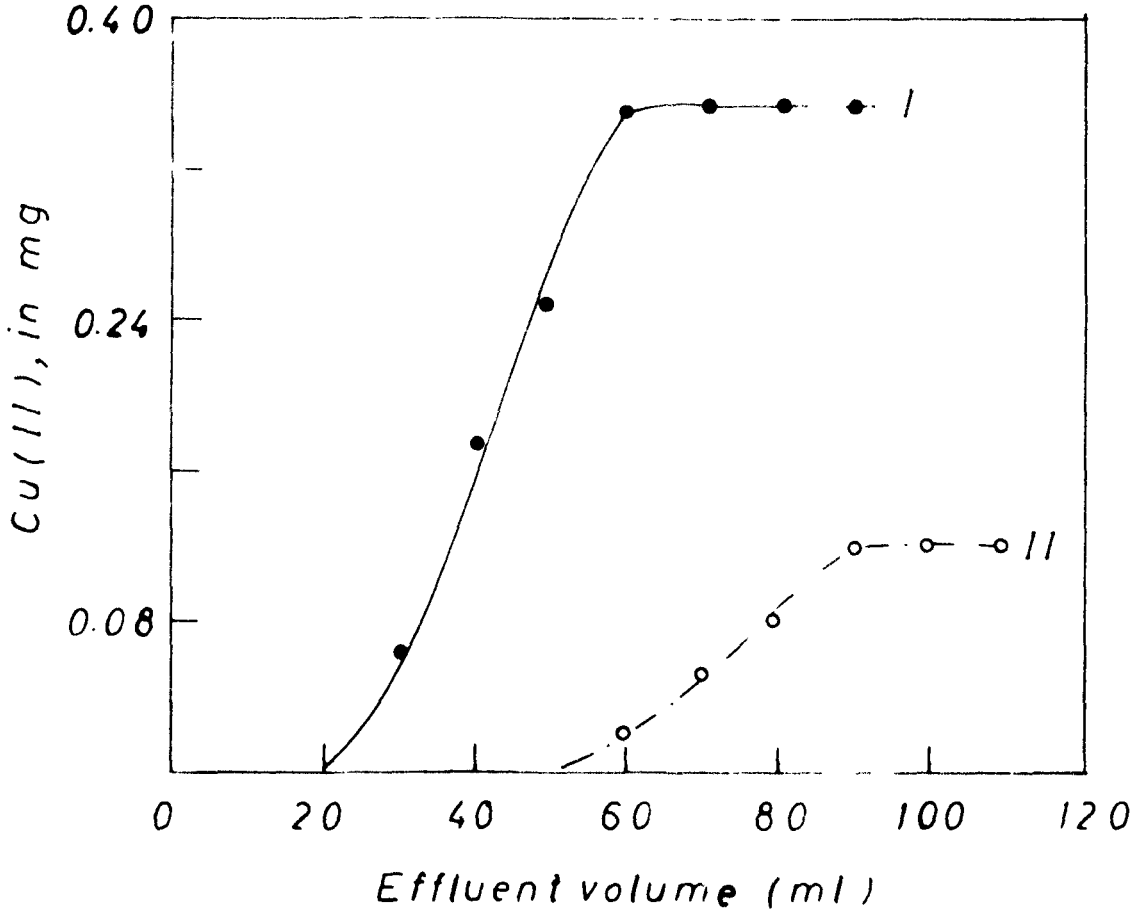


Fig. 17 Break Through Curves

I, Cu(II) conc.^{n} 0 38 mg / bed volume

II, Cu(II) conc.^{n} 0.19 mg / bed volume

TABLE 33

BREAK THROUGH CAPACITY OF STANNICDIETHANOLAMINE

Concentration of feed solution = 0.385 mg/10 ml

pH of the solution = 6.0

Flow rate = 0.5 ml/min.

Fractions (ml)	Cu(II) in effluent, (mg)
10	0.00
20	0.00
30	0.064
40	0.184
50	0.246
60	0.353
70	0.353
80	0.353

TABLE 5A

BREAK THROUGH CAPACITY OF STANNICDIETHANOLAMINE

Concentration of feed solution = 0.192 mg/10 ml

pH of the solution = 6.0

Flow rate = 0.5 ml/min.

Fractions, (ml)	Cu(II) in effluent, (mg)
10	0.00
20	0.00
30	0.00
40	0.00
50	0.00
60	0.021
70	0.050
80	0.083
90	0.140
100	0.140

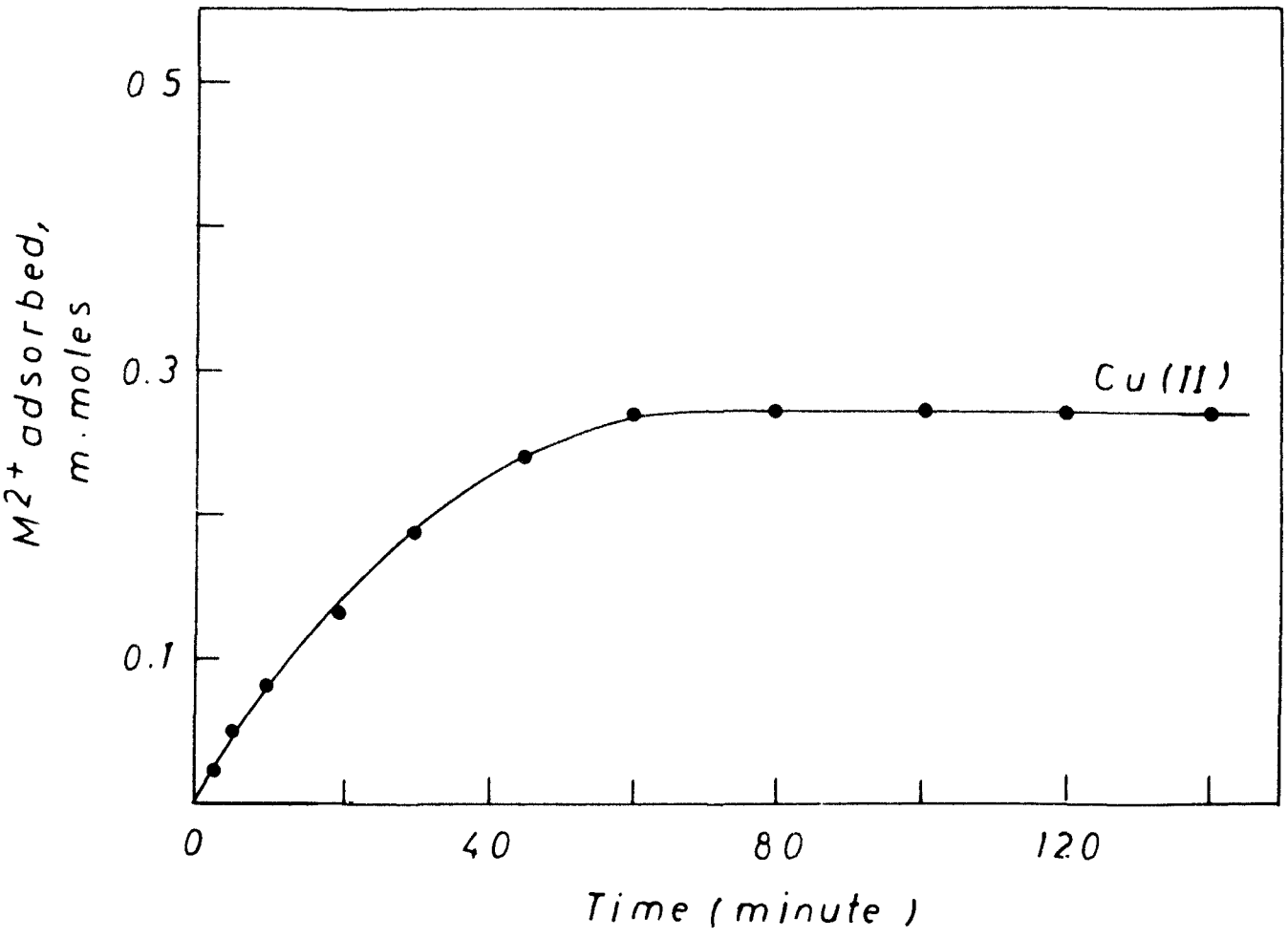


Fig. 18 Rate of sorption of Cu (II) at pH 6

Rate of Sorption: Rate of sorption was determined by a batch process. 0.022 m.mole of Cu(II) ions in a solution of pH 6 was shaken with 500 mg of stannic diethanolamine at different intervals of time and amount of unsorbed ions was then determined in the supernate. The results are summarised in table 35 and plotted in figure 18.

TABLE 35

RATE OF SORPTION OF Cu(II) AT pH 6

Time, (minutes)	Initial amount of Cu(II), (m.moles)	Amount of Cu(II) adsorbed, (m.moles)
0	0.35	0.00
2	0.35	0.01
5	0.35	0.05
10	0.35	0.08
20	0.35	0.13
30	0.35	0.19
45	0.35	0.24
60	0.35	0.27
90	0.35	0.27
120	0.35	0.27

Separations: Separations were done on 30 x 0.39 cm^2 glass columns. 2.0 g of the exchanger was taken on a glass wool support of the column and washed with a solution of pH 6 buffer. Solutions of metal ions

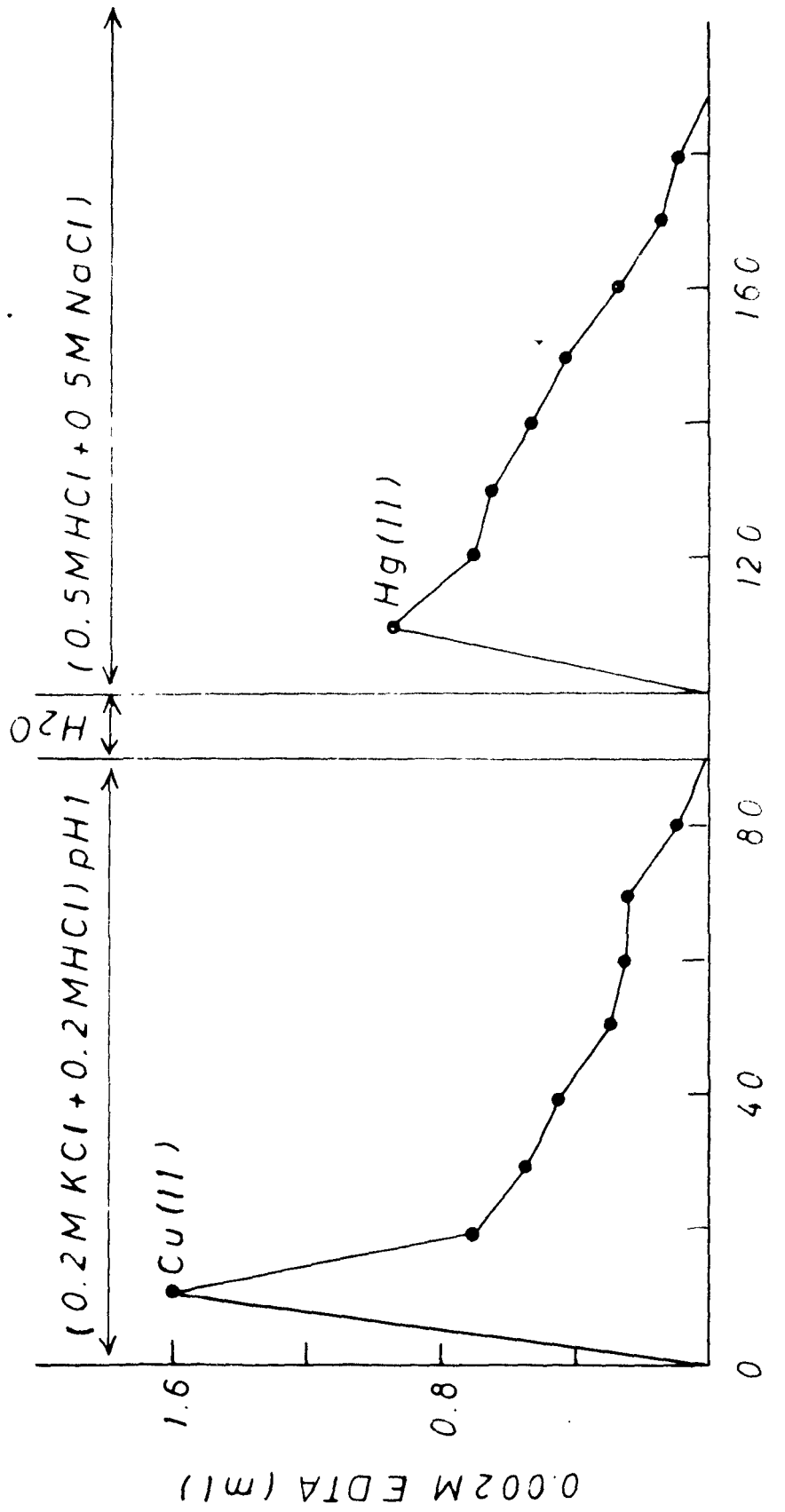


Fig. 19 Separation of Hg(II) - Cu(II)

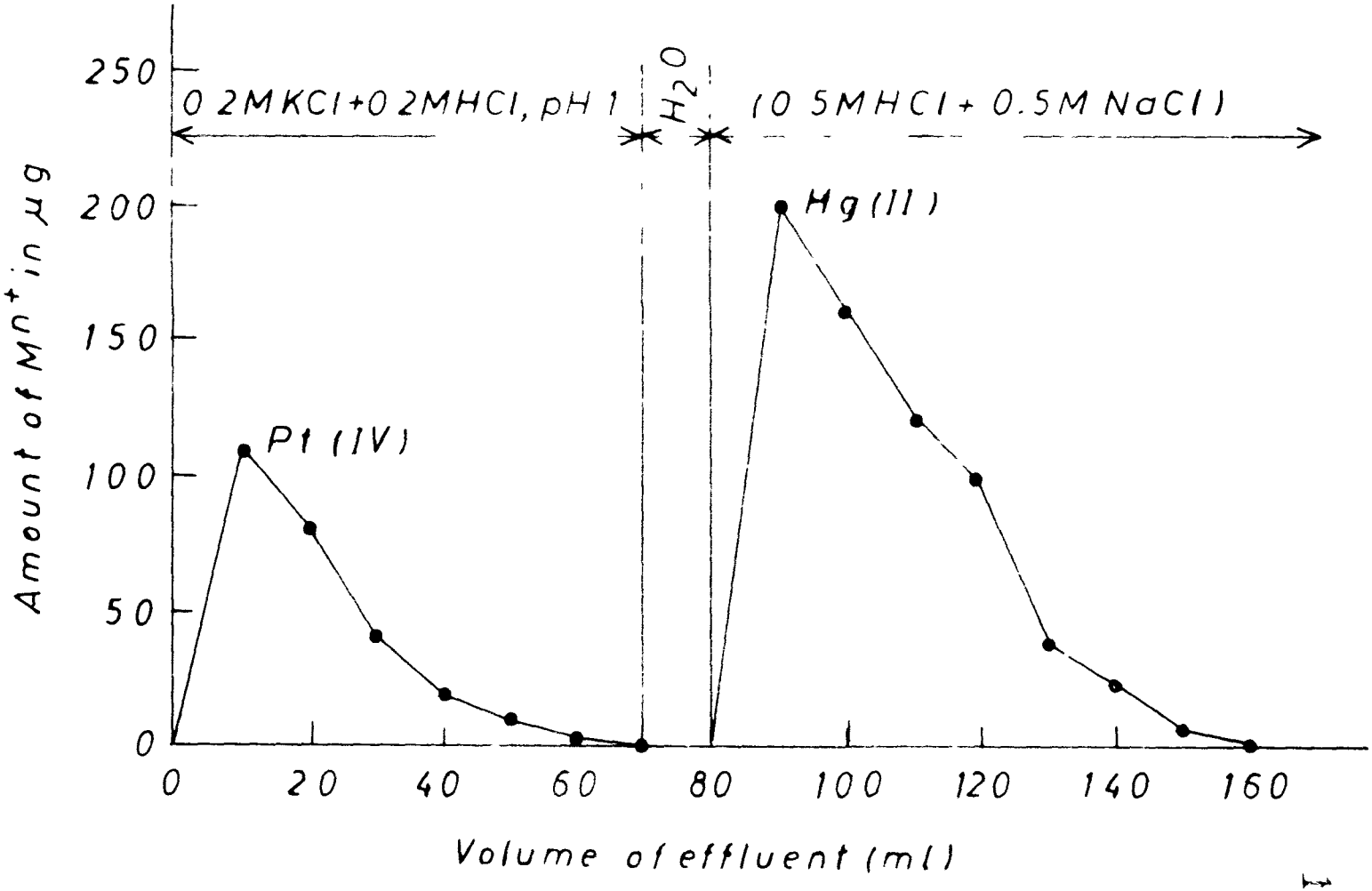


Fig. 20 Separation of Pt (IV) from Hg (II)

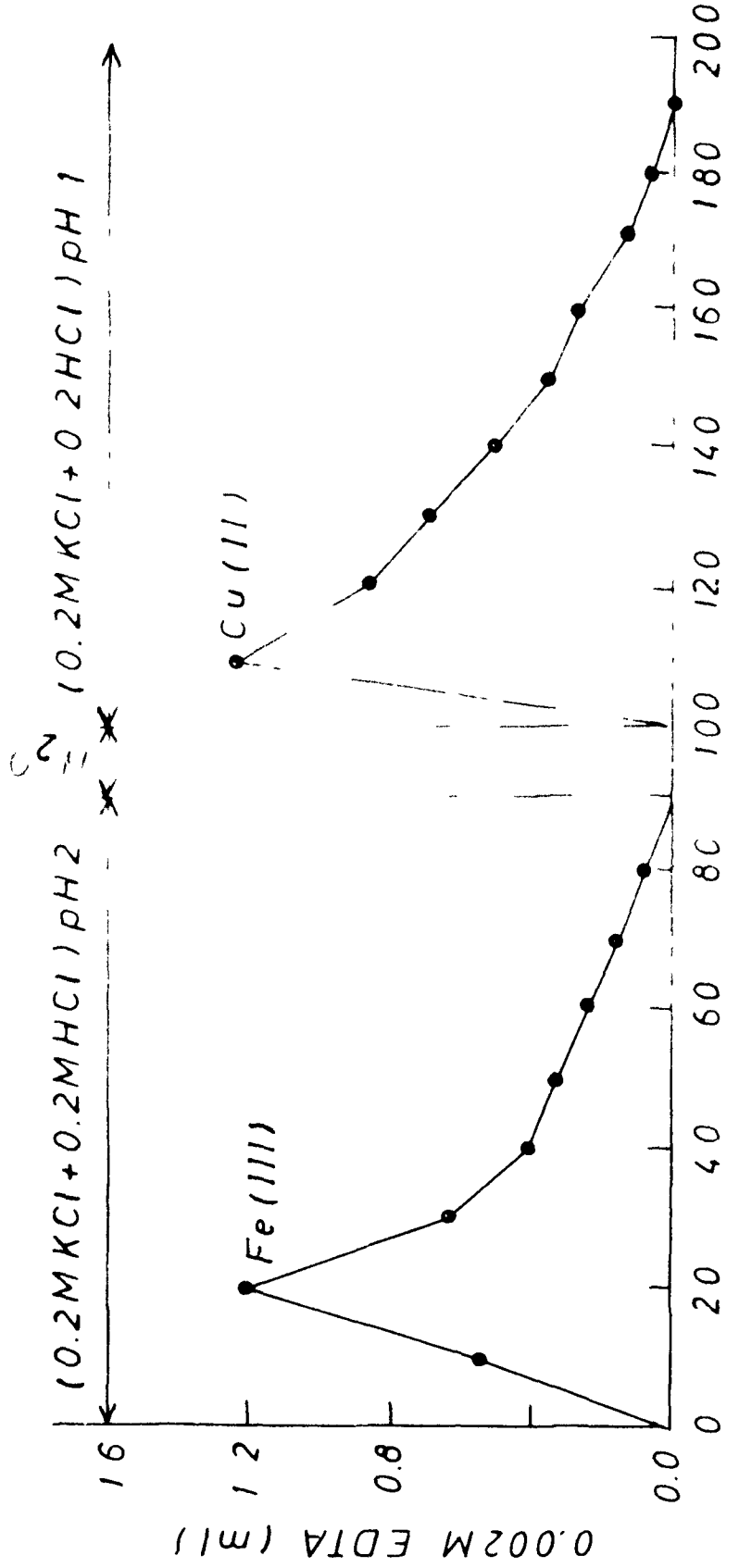


Fig.21 Separation of Fe (III) - Cu (II)

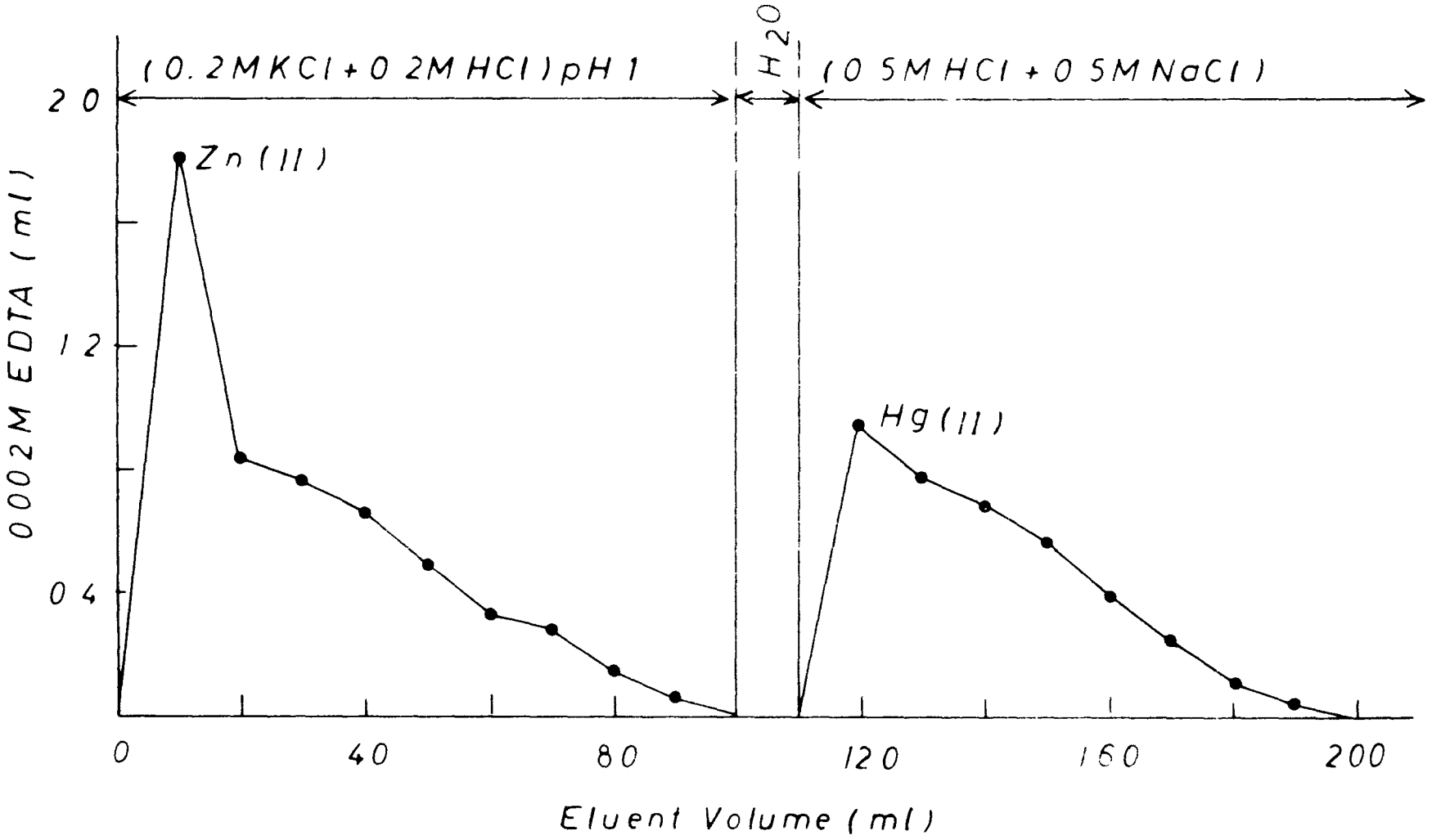


Fig 22 Separation of Hg (II) - Zn (II)

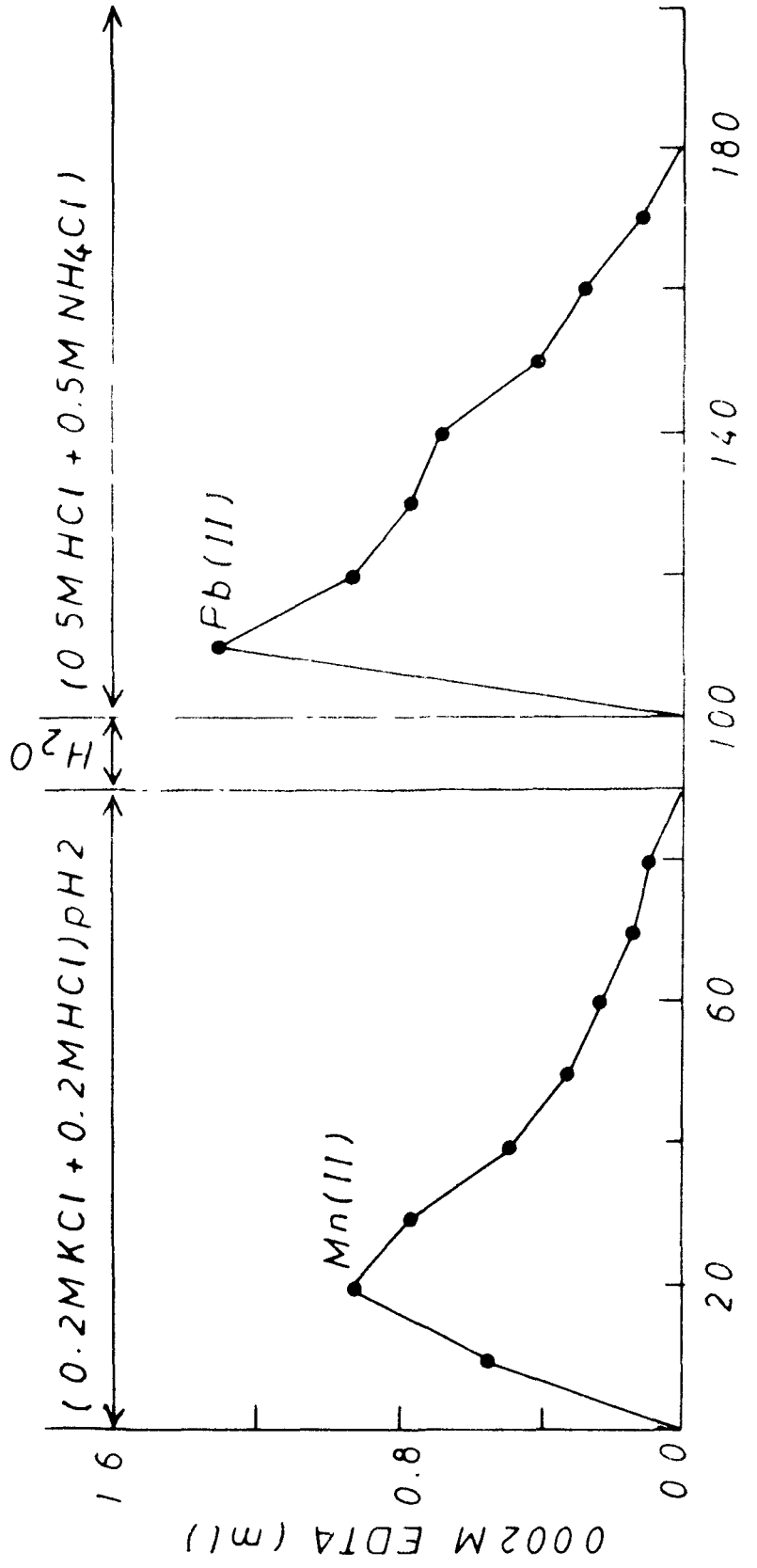


Fig 23 Separation of Pb(II) - Mn(II)

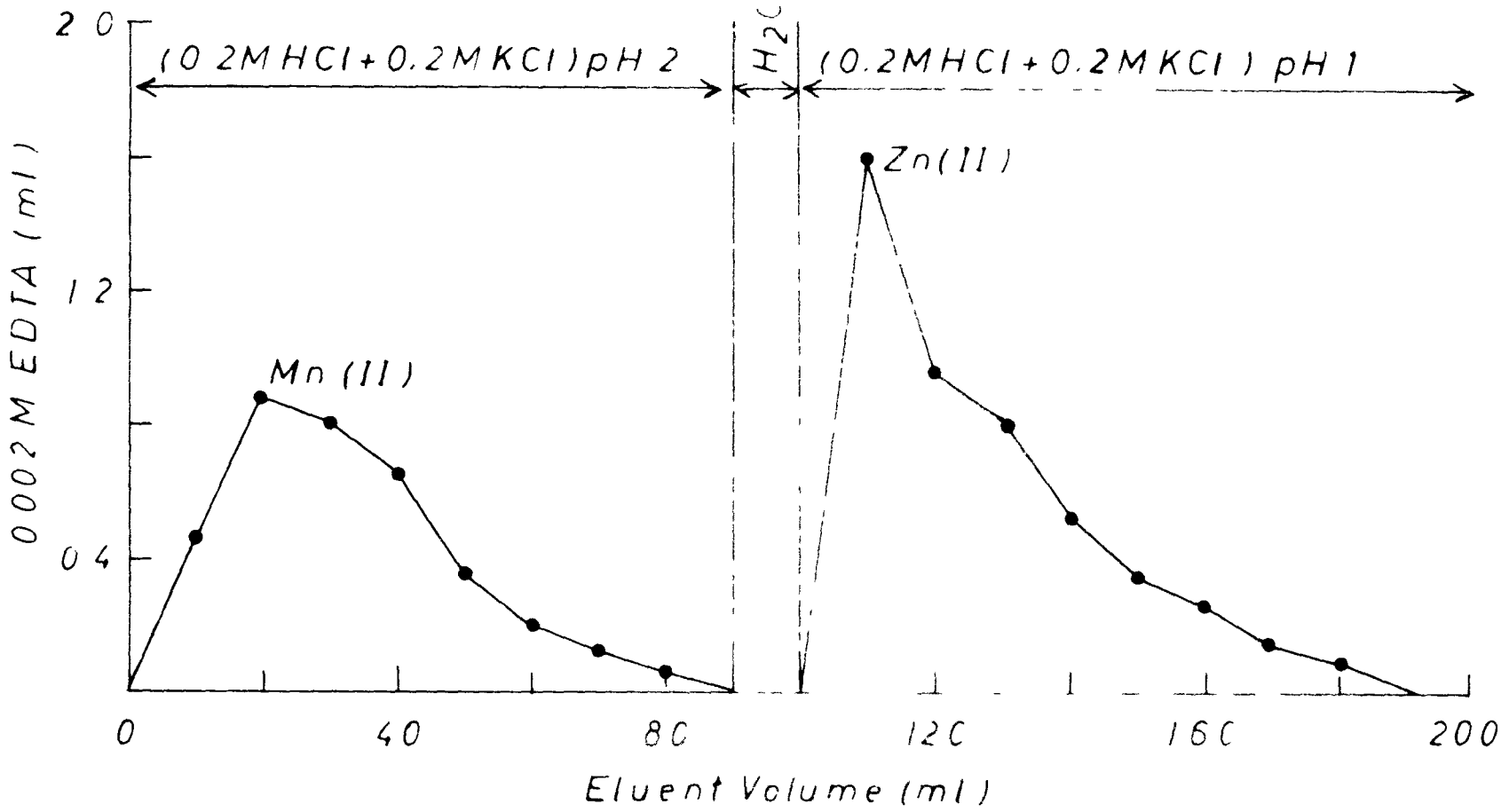


Fig 24 Separation of Mn (II) - Zn (II)

to be separated were then allowed to trickle down the column at a flow rate of 0.5 ml min^{-1}. The results of the separations achieved and eluents used are presented in table 36. Order of elution is shown in figures 19, 20, 21, 22, 23 and 24.

TABLE 36

QUANTITATIVE SEPARATIONS OF METAL IONS ON STANNIC DIETHANOLAMINE

Sl. No.	Separations achieved	Eluents	Eluent volume (ml)	Amount loaded (µg)	Amount found (µg)	% Error
1.	Cu(II)	(0.2M KCl + 0.2M HCl) pH 1	80	490	483	1.40
	Hg(II)	(0.5M HCl + 0.5M NaCl)	80	510	505	0.99
2.	Pt(IV)	(0.2M KCl + 0.2M HCl) pH 1	60	425	422	0.70
	Hg(II)	(0.5 HCl + 0.5M NaCl)	80	510	508	0.40
3.	Fe(III)	(0.2M KCl + 0.2M HCl) pH 2	90	560	552	1.40
	Cu(II)	(0.2M KCl + 0.2M HCl) pH 1	80	490	476	3.04
4.	Zn(II)	(0.2M KCl + 0.2M HCl) pH 1	90	500	508	1.60
	Hg(II)	(0.5M HCl + 0.5M NaCl)	80	510	508	1.50
5.	Mn(II)	(0.2M KCl + 0.2M HCl) pH 2	90	410	400	2.40
	Pb(II)	(0.2M HCl + 0.5M NH_4Cl)	70	625	600	0.80
6.	Zn(II)	(0.2M HCl + 0.2M KCl) pH 1	90	500	496	0.80
	Mn(II)	(0.2M HCl + 0.2M KCl) pH 2	90	410	404	1.46

DISCUSSION

As is evident from table 28 precipitation of stannic diethanolamine occurred only when metal to amine ratio was maintained at 1:2. Any variation in this ratio resulted in disappearance of the precipitate. It is worthmentioning that stannic diethanolamine does not show any ion exchange capacity. When stannic diethanolamine in H^+ form was kept in contact with a solution of sodium nitrate no release of H^+ ions was observed. Similar experiment with stannic diethanolamine in Cu^{2+} form too failed to show any ion exchange capacity. The exchanger, however, possesses an appreciable sorption capacity. Metal ions from the solutions of pH 3 to pH 6 are taken up by the exchanger and released when pH of the column was brought down to less than this range. The inability of stannic diethanolamine to show any ion exchange property reveals that there is no fixed negative or positive charge with the exchanger. Sorption of metal ions occurs because of the presence of nitrogen atom of amine group that offers sites for the chelation with the metal ions. Since stability of the metal-ligand depends upon the pH of the solutions, any variation in pH leads to detachment of metal from the ligand. Sorption capacity of stannic diethanolamine was found to be 0.55 m.moles g^{-1}. The exchanger acquired the colour of the sorbed metal ions which can be conspicuously seen. The visible colour change due to sorption of different metal ions is shown in table 37.

TABLE 37

COLOUR CHANGE DUE TO SORPTION

Sl. No.	Metal ion sorbed	Colour of the exchanger
1.	Cu^{2+}	Blue
2.	Fe^{3+}	Brown
3.	Cd^{2+}	No change
4.	Ni^{2+}	Green
5.	Zn^{2+}	No change
6.	Co^{2+}	Pink
7.	Pb^{2+}	No change
8.	Pt^{4+}	Light yellow

The extent to which stannic diethanolamine dissolves in different acids and bases is reported in table 30. It can be seen that it is fairly stable in acids upto 2M and in ammonium hydroxide upto 6M. Sodium hydroxide, however, is detrimental and as dilute a solution as 1M reduces the stability to a greater extent. This is because sodium hydroxide releases diethanolamine from the exchanger.

The results of composition studies show that stannic and

diethanolamine are present in the molar ratio of 1:2.221.

The results of IR spectrum of stannic diethanolamine presented in figure 15 show the following pattern:

(i) A broad peak ranging from 3000 to 3500 cm^{-1}; maximum at 3300 is attributed to N-H stretching frequency.

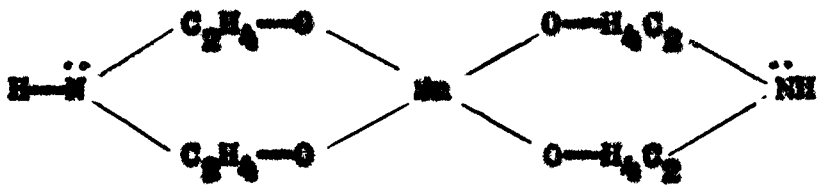
(ii) A peak around 720 cm^{-1} resembles with N-H rocking frequency.

(iii) A peak at 1620 cm^{-1} is due to N-H bending.

(iv) A diffused peak around 1420 may be due to the presence of $-CH_2$ group.

(v) Another peak around 930 may be due to C-H group.

On the basis of first three points it can be said that the compound precipitated by stannic chloride and diethanolamine still retains the N-H group. Furthermore, the frequency of OH group is not clear, therefore, on the basis of the results of i.r. and composition determination of the product giving Sn:amine ratio as approximately 1:2, the structure of the compound may be proposed as follows:



The linking of Sn with O of OH group and not with N of N-H group is confirmed by the fact that by mixing stannic chloride and diethylamine, no precipitate was obtained. The above structure gives the availability of the lone pair at nitrogen to be used for

coordination with metal ions and this forms the basis of this compound working as a chelate ion exchanger.

The results of the study of the sorption behaviour of eight metal ions in solutions of different pH are presented in figure 16. The behaviour of these metal ions can be described into three groups:

(i) Metal ions that stay with the exchanger at all pH, viz. Hg(II) and Pb(II).

(ii) Metal ions that are less sorbed at pH 1, such as Pt(IV), Cu(II), Ni(II), Zn(II) and Cd(II).

(iii) Metal ions that are not at all sorbed at pH 1 and pH 2, namely Fe(III) and Mn(II).

A high affinity for Hg(II) and Cu(II) are, generally, the characteristic of resins containing sulphur and nitrogen atoms as ligands (11-13). Hence it is the presence of nitrogen atoms in stannic diethanolamine which is responsible for its high selectivity for Hg(II) and though to a lesser degree, for Cu(II). Sorption of Fe(III) seems to occur not because of its chelation with nitrogen atom but due to its chelation with oxygen of diethanolamine. Fe(III) prefers to coordinate through oxygen atom than through nitrogen atom (14)

Because of the difference in behaviour of different metal ions in solutions of different pH, a number of separations were possible. Successful separations of Hg(II) from Cu(II) and Zn(II); Pb(II) from Mn(II); Cu(II) from Fe(III) and Pt(IV); and Zn(II) from Mn(II) have been achieved. Table 36 summarizes the number of separations achieved. Eluents used and order of elution is given in figures 19, 20, 21, 22, 23 and 24.

Shown in figure 17 are the break through curves for Cu(II) at different concentrations. These studies reveal that about 40 bed volumes in case of 0.38 mg per bed volume and 60 bed volumes in case of 0.192 mg per bed volume of feed solutions can be passed through the exchanger without any leakage of Cu(II) ions into the effluent. Further the higher concentration of Cu(II) ions gives sharper break through.

Figure 18 shows rate of sorption of Cu(II) in a solution of pH 6. It can be seen that 20 minutes are required for 50% uptake of Cu(II) ions and equilibrium is reached within 60 minutes. Normally this fast equilibration rate is not expected from inorganic ion exchangers. Presence of amino group (a chelation site) in stannic diethanolamine is responsible for such a fast equilibration rate. This further shows that organometallic exchangers too function like their organic counterparts inasmuch as rate of sorption is concerned. However, equilibration studied were made by shaking the material with a particular cation solution for four hours to ensure the equilibrium.

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C H A P T E R - VI

SPECTROPHOTOMETRIC DETERMINATION OF VANADIUM(V) WITH BRUCINE

CHAPTER - VI

SPECTROPHOTOMETRIC DETERMINATION OF VANADIUM(V) WITH BRUCINE

The spectrophotometric determination of vanadium(V) has been drawing considerable attention recently (1). The important reagents used are o-phenylenediamine (2), thiosalicylamide (3) and tropolone (4). Some other methods have also been reported recently (5-8). Every methods has its advantages and limitations. The method using o-phenylenediamine and 8-hydroxyquinoline are susceptible to number of interferences, while the method using N-(P-N, N-dimethylaniline-3-methoxy-2-naphtho) hydroxamic acid ($CHCl_3$) is very sensitive but platinum and iridium can be tolerated only upto a limit. We observed a new colour reaction between vanadium(V) and brucine in acidic medium. Therefore, it was proposed to develop this reaction for the determination of vanadium(V). The method developed is simple, highly selective and sufficiently sensitive. Most of the metal ions that are commonly associated with vanadium(V) do not interfere. The method is suitable for the determination of vanadium(V), particularly in the presence of Ti(IV) which interferes seriously in most of the other recommended procedures. The present report summarizes our studies on this reaction to develop a method for the determination of vanadium(V).

EXPERIMENTAL

Apparatus: A Metner spectra 75' spectrophotometer was employed for the absorbance measurements.

Reagents and Solutions

Standard vanadium(V) solution: A standard solution of vanadium(V) was prepared by dissolving 0.771 g of analytical grade ammonium metavanadate in 100 ml of water. The metal content was estimated titrimetrically with standard permanganate solution. One ml of this solution contain 510 µg of vanadium(V).

Brucine solution: 1% w/v solution of brucine was prepared by dissolving it in distilled ethanol. This solution could be kept without change for about a month at room temperature.

All other chemicals were of Analytical grade.

Recommended Procedure: An aliquot of vanadate solution containing 85 to 408 µg of vanadium was taken and to this was added 1 ml of 1% brucine and 2.5 ml of 12M HCl. The solution was then diluted to 25 ml with distilled water. The absorbance was read at 365 nm against the reagent blank.

In cases where 5-20 µg of vanadium were employed the measurements were made by keeping the final volume upto 10 ml.

RESULTS

To develop the optimum conditions for the reaction between brucine and vanadium(V) the effect of various factors was studied.

Absorption Spectra: Vanadium(V) gives a yellow colored complex with brucine in acidic medium. The absorption spectrum of the complex and the corresponding data are given in table 38 and shown in figure 25.

TABLE 38

ABSORPTION AT DIFFERENT WAVE LENGTH

12M HCl = 2.5 ml

1% Brucine = 1 ml

Vanadium = 40 ppm

Wave length	Absorbance
350	0.38
355	0.35
360	0.38
365	0.39
370	0.38
375	0.31
380	0.25
390	0.20

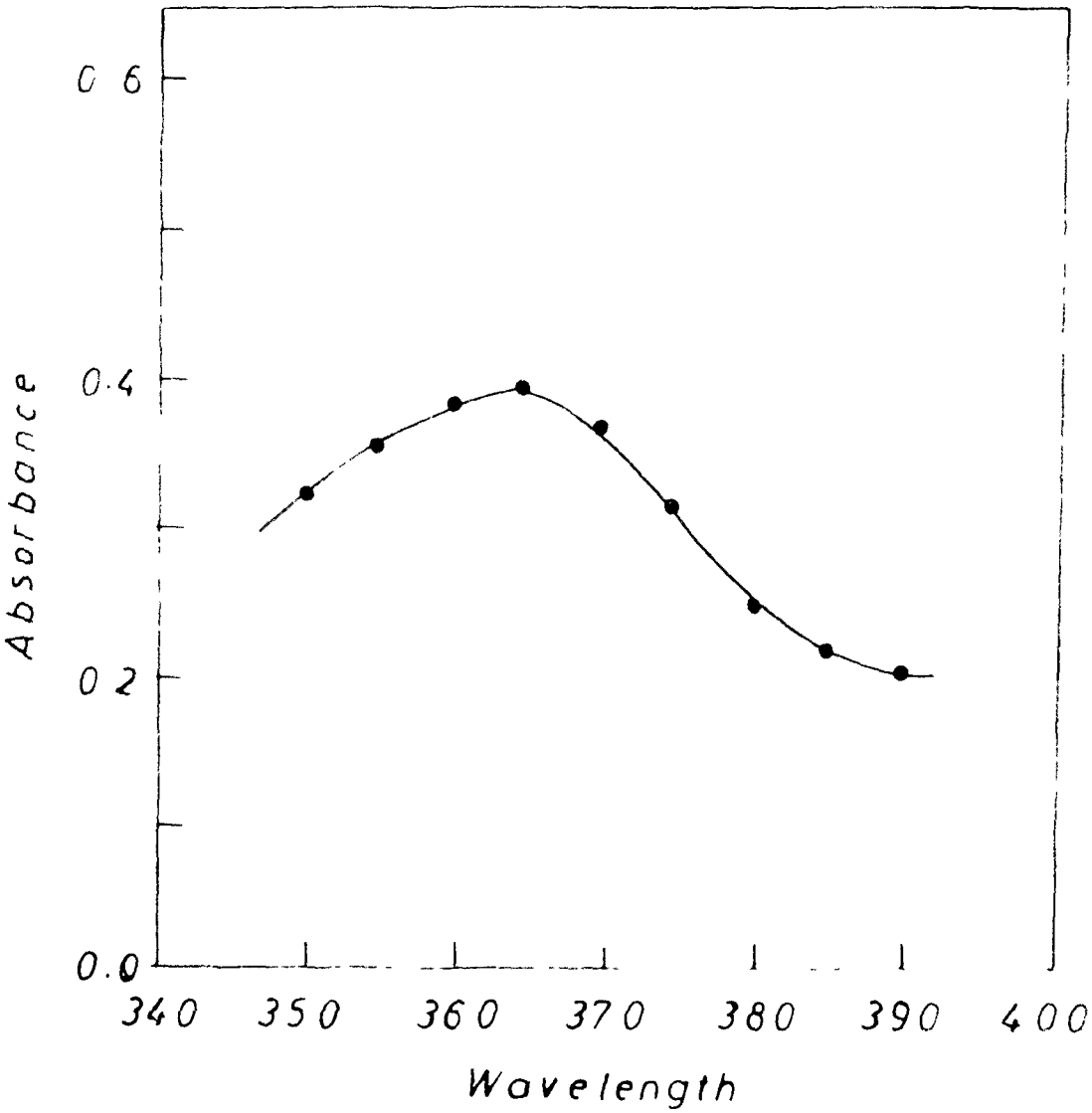

Fig. 25 Absorption spectrum of different wavelength

Effect of Acid Concentration: The effect of pH was studied by adding hydrochloric acid of different normalities to a solution containing 40 ppm of vanadium and 1 ml of 1% brucine and making the final volume upto 25 ml. The results are plotted in figure 26 and given in table 39.

TABLE 39

EFFECT OF ACID STRENGTH

Vanadium(V) = 40 ppm

Brucine = 1 ml

12M HCl = x ml

12M HCl, x (ml)	Absorbance, at 365 nm
1.0	0.16
2.5	0.18
4.0	0.15
5.0	0.15

Effect of Reagent Concentration: The amount of brucine also affects the colour reaction. A study of its effect on colour intensity was made by adding different amounts of brucine to 40 ppm of vanadium solution. 2.5 ml of 12M HCl was added to the reaction mixture and

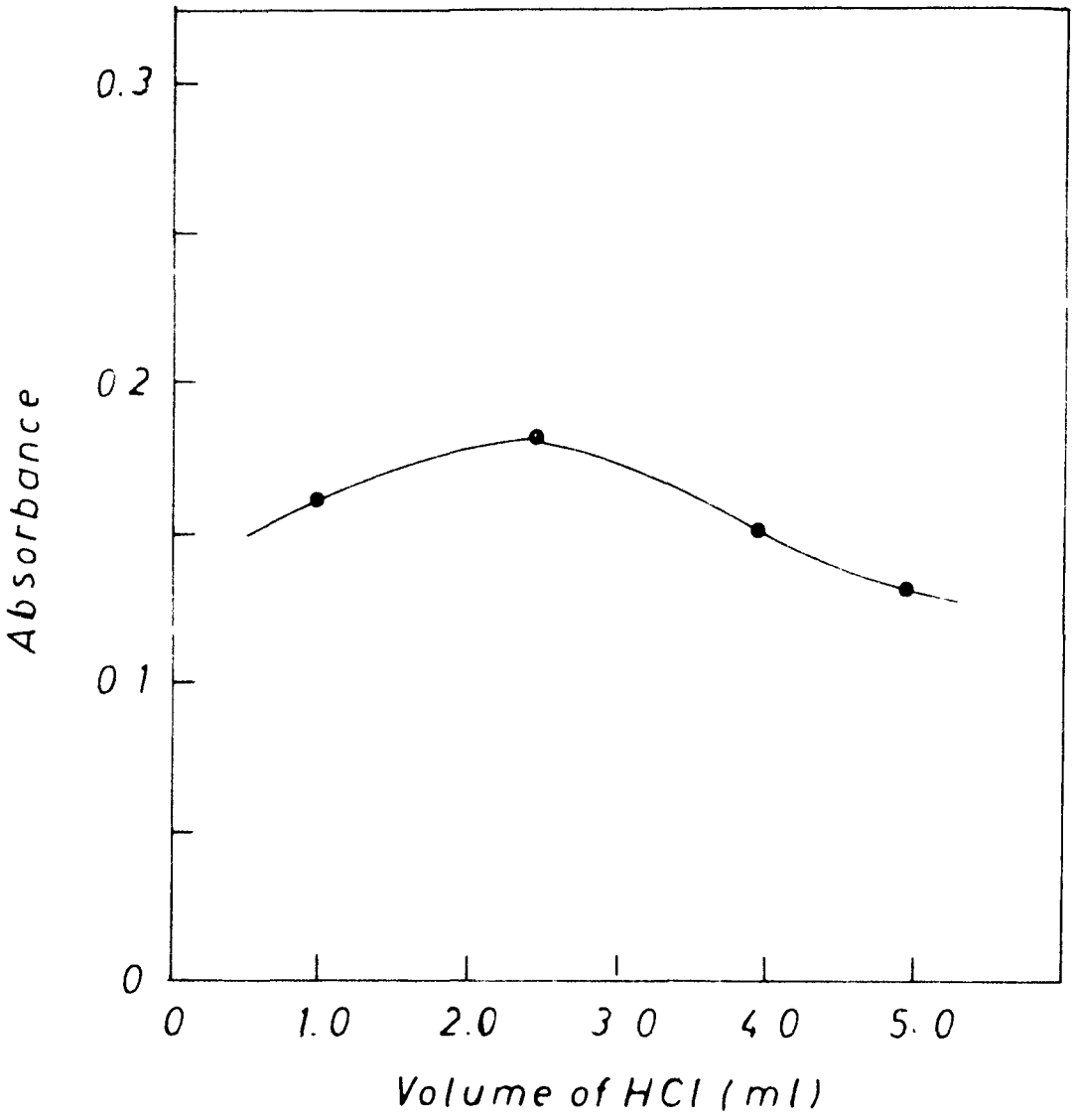

Fig. 26 Effect of HCl concentration on the absorbance of yellow coloured complex

total volume was made upto 25 ml with water. The results are presented in table 40.

TABLE 40

EFFECT OF BRUCINE CONCENTRATION ON INTENSITY OF COLOUR AT 365 nm

Vanadium (0.01M), (ml)	Brucine (0.01M), (ml)	Absorbance
0.6	0.05	0.50
0.6	0.10	0.52
0.6	0.20	0.58
0.6	0.30	0.58
0.6	0.40	0.57
0.6	0.50	0.56

Effect of Time: To study the effect of time on the intensity of colour, absorbance of the complex was noted at different intervals of time.

Composition of the Complex: The composition of the vanadium brucine complex was established by Job's method and molar ratio method. For these methods, 0.01M solutions of vanadium and brucine were used. In Job's method a total volume of 2 ml of complimentary mixtures

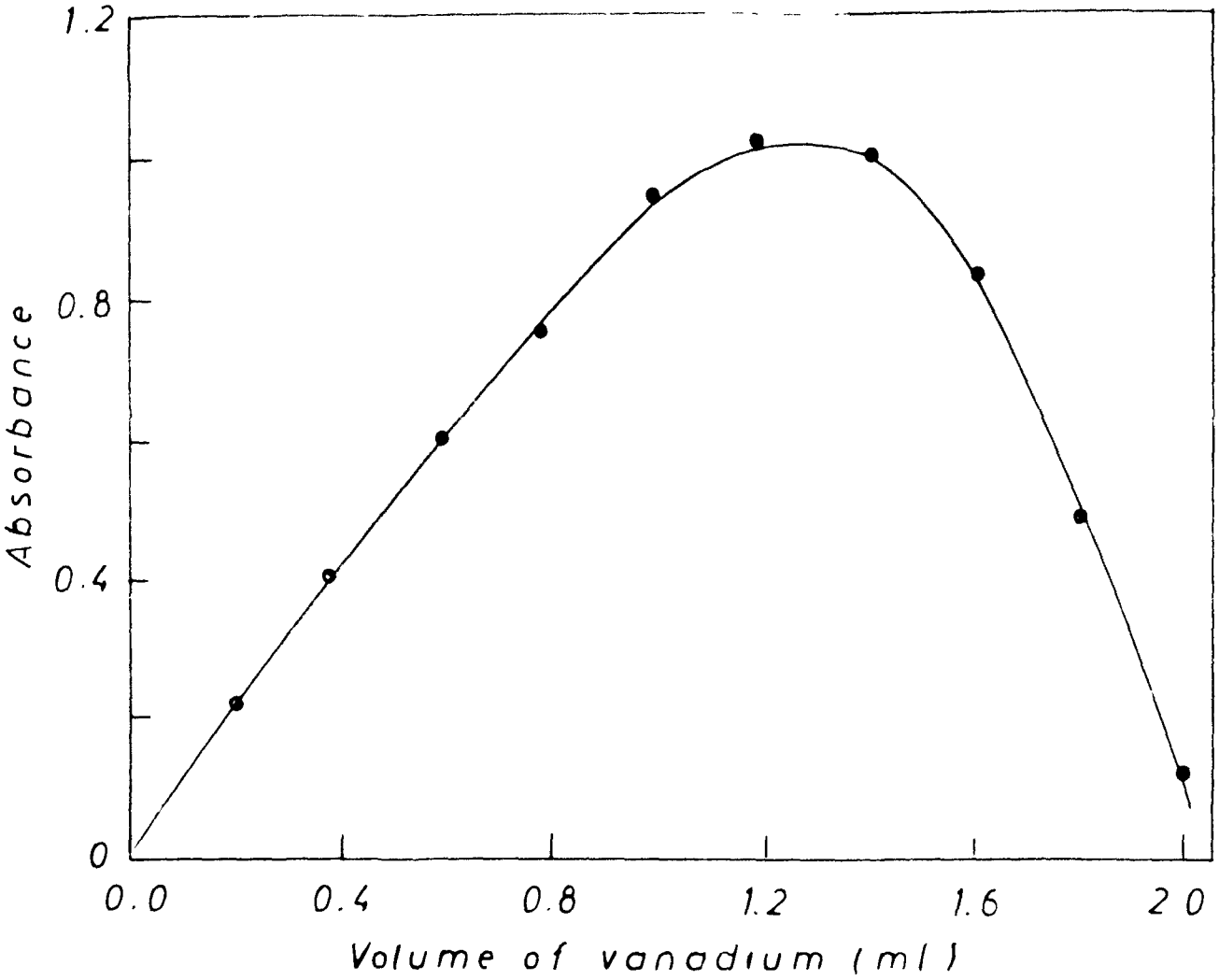

Fig. 27 Continuous variation plot for vanadium-brucine complex.

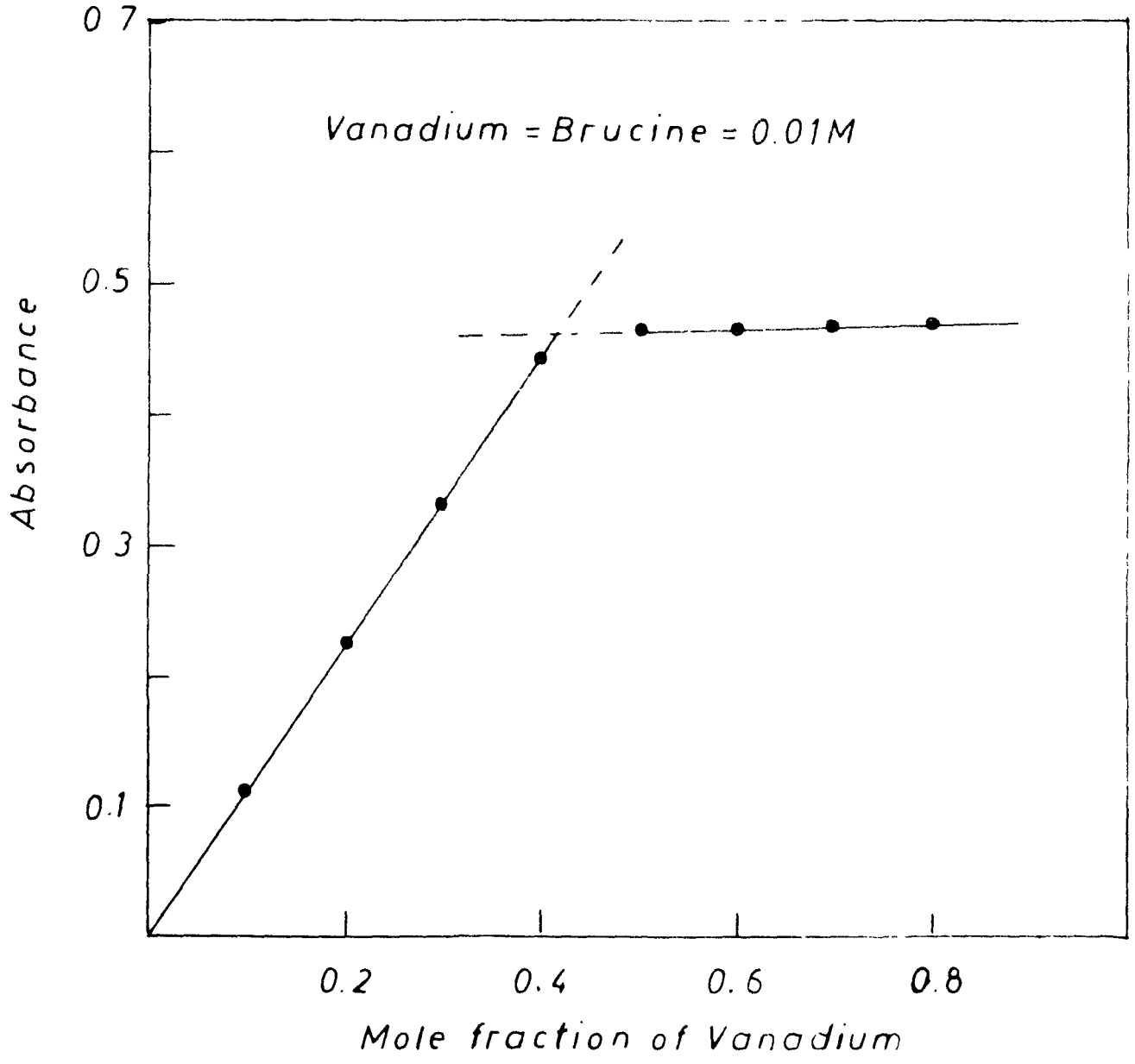

FIG.28 Mole ratio plot for vanadium brucine complex

containing vanadium and brucine were diluted to 25 ml and measured the absorbance at 365 nm (table 41). A graph was plotted with mole fraction of vanadium as abscissa and absorbance as ordinate (Fig.27). The maxima in the curve corresponds to mole fraction of 1.33 with respect to vanadium and 0.67 with respect to brucine. In mole ratio method, concentration of the reagent is fixed and that of vanadium(V) is varied. The results are shown in figure 28 and table 42.

TABLE 41

JOB'S METHOD

Vanadium(V) = Brucine = 0.01M

12M HCl = 2.5 ml

Wave length = 365 nm

Vanadium, (ml)	Brucine, (ml)	Absorbance
0.0	0.0	0.0
0.2	1.8	0.21
0.4	1.6	0.37
0.6	1.4	0.60
0.8	1.2	0.74
1.0	1.0	0.94
1.2	0.8	1.15
1.4	0.6	1.10
1.6	0.4	0.84
1.8	0.2	0.42
2.0	0.0	0.12

TABLE 42

MOLE RATIO METHOD

Vanadium = Brucine = 0.01M

Brucine = 0.2 ml

12M HCl = 2.5 ml

Wave length = 365 mm

Vanadium, (ml)	Absorbance
0.00	0.00
0.10	0.11
0.20	0.22
0.30	0.33
0.40	0.42
0.45	0.46
0.50	0.46
0.60	0.46

Optimum range, Sensitivity and photometric error: Keeping above factors in view the recommended procedure was set to determine vanadium in the range 5 µg to 408 µg and the absorbance was recorded for various amounts of vanadium. The results are plotted in figure 29. The sensitivity of the method may be calculated for the lowest value of absorbance 0.01 (as can be read from the spectrophotometer

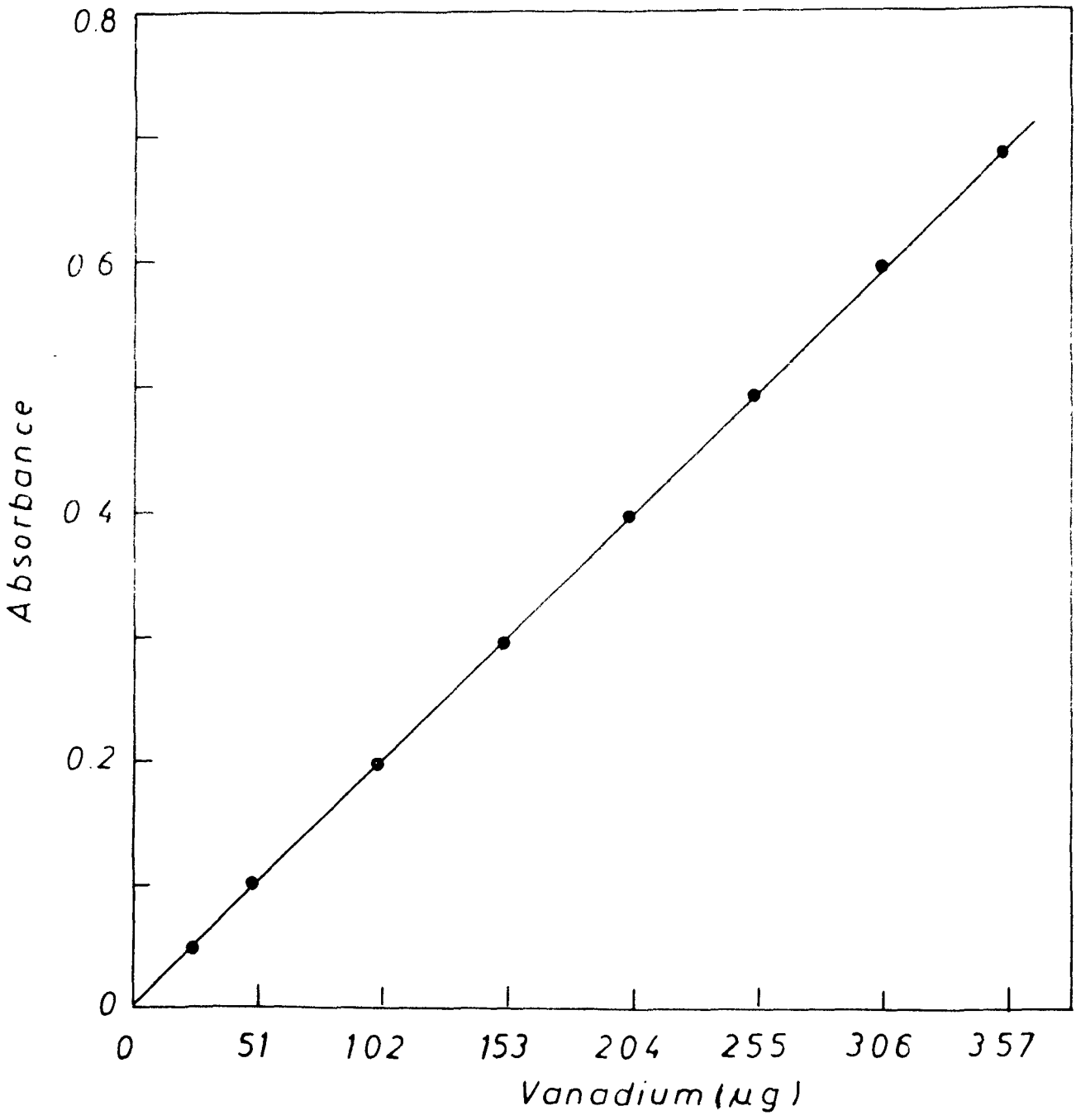

Fig. 29 Calibration curve of vanadium

employed). The sensitivity thus obtained was 0.21 ppm. The results of nine replicate determinations are presented in table 43.

TABLE 43

STANDARD DEVIATION

1% Brucine = 1 ml

Vanadium = 204 µg

12N HCl = 2.5 ml

Vanadium, (ml)	Absorbance	% standard deviation
0.4	0.38	
0.4	0.39	
0.4	0.39	
0.4	0.38	
0.4	0.38	1.5
0.4	0.37	
0.4	0.37	
0.4	0.38	
0.4	0.38	

Effect of Diverse ions: The applicability of the method was checked for the determination of vanadium in presence of a large number of diverse ions taken as nitrates and chlorides. The metal ions that

do not interfere even in 250 fold excess is shown in table 44 and those that did not interfere upto 100 fold excess is shown in table 45.

TABLE 44

DETERMINATION OF VANADIUM IN PRESENCE OF SOME FOREIGN IONS

Amount of vanadium taken = 204 µg/ml

1% brucine = 1 ml

12M HCl = 2.5 ml

Ion	Amount of foreign ion added, (mg)	Amount of vanadium found, (µg)	% Error
None	50	204	0.0
Al^{3+}	50	209	2.5
Pb^{2+}	50	204	0.0
Cr^{3+}	50	204	0.0
Ti^{4+}	50	200	2.0
Sm^{3+}	50	109	2.5
Tb^{3+}	50	204	0.0
Dy^{3+}	50	209	2.5
Nd^{3+}	50	207	0.0
Pr^{3+}	50	204	0.0
Ho^{3+}	50	209	2.5
La^{3+}	50	209	2.5
In^{3+}	50	200	2.0
Gd^{3+}	50	200	2.0
Ni^{2+}	50	204	0.0

TABLE 45

DETERMINATION OF VANADIUM IN PRESENCE OF SOME FOREIGN IONS WITHIN TOLERABLE LIMITS

Amount of vanadium taken = 204 mg per 10 ml

Ions	Tolerance limit, (mg)	Vanadium found, (mg)	% Error
None	-	204	0.0
Zr^{4+}	30	204	0.0
Fe^{3+}	25	209	2.5
Co^{2+}	20	206	0.9
Cu^{2+}	20	200	2.0
Mo^{6+}	20	204	0.0
Ce^{4+}	20	204	0.0
Mn^{2+}	30	209	2.5
Th^{4+}	25	209	2.5

DISCUSSION

The yellow coloured complex formed by the reaction of brucine with vanadium(V) in acidic medium gives the maximum absorption at 365 nm. It is evident from figure 26 that a variation in acid concentration affects the colour intensity. Maximum intensity of the colour was obtained at the acid concentration of 1N to 1.5N. Nitric acid was found to attack the reagent and therefore could not be used.

The amount of brucine also affects the colour reaction. A study of its effect on colour intensity as shown in table 40 show that the absorbance increased with the concentration of brucine till brucine concentration was half of the concentration of vanadium. Further increase in brucine concentration had no effect on the intensity of the colour indicating that reaction takes place in the brucine-vanadium ratio of 1:2. A study of the effect of time shows that colour intensity of the complex was not affected even after being kept for two days at room temperature.

The results of the composition determination plotted in Figures 27 and 28 clearly show that two moles are required for 1 mole of brucine. The calibration curve shown in figure 29 is a straight line passing through the origin showing the applicability of Beer's law within the optimum range. The molar absorptivity was 2.4×10^3. The results of nine replicate determinations presented in table 43 indicate that the method is reproducible and percent standard deviati was 1.5. In order to check the accuracy four unknowns were tried - the average error was 2.2%.

A study of the effect of diverse ions reveals that most of the metal ions that are commonly associated with vanadium(V) do not interfere with its determinations even in 250 fold excess as shown in table 44. The ions that interfere when present in more than 100 fold excess are shown in table 45; interference of Fe^{3+} was removed by masking it with phosphate, Mo(VI) was removed by extracting it with palmitic acid and tributylphosphate. Interference of Ce^{4+} was got rid of by first extracting the vanadium with tributylphosphate in presence of HCl and then back extracting it with water. The same method could be employed for every interfering metal ion when they are present in beyond their tolerance limit as given in table 45.

On the basis of above discussion it becomes clear that the reaction of brucine with vanadate can be used for the determination of vanadium in ppm range in presence of common interfering ions. The precision and accuracy is within the acceptable range.

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SYNTHESIS OF ZIRCONIUM PHOSPHOIODATE AND ITS USE AS AN ELECTRON-ION-EXCHANGER

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Summary. — A new inorganic ion exchanger, zirconium phosphoiodate, has been prepared and utilised for studying oxidation reactions. Its ion-exchange and electron-exchange properties have been investigated. Analytical applications have been developed and the oxidation of iron(II), titanium(III), arsenic(III), tin(II), and antimony(III) to iron(III), titanium(IV), arsenic(V), tin(IV) and antimony(V), respectively, have been achieved quantitatively. The mechanism of oxidation is discussed.

Riassunto — È stato preparato, e impiegato per lo studio di reazioni di ossidazione, un nuovo scambiatore di ioni inorganico, il fosfoiodato di zirconio. Oltre a studiare le sue proprietà di scambiatore di ioni e di scambiatore di elettroni, sono state messe a punto alcune applicazioni analitiche. Con questo scambiatore è possibile ossidare quantitativamente il ferro(II), il titanio(III), l'arsenico(III), lo stagno(II) e l'antimonio(III) rispettivamente a ferro(III), titanio(IV), arsenico(V), stagno(IV) e antimonio(V). Viene discusso il meccanismo dell'ossidazione.

The analytical applications of ion exchangers are important and new uses are being actively developed. Oxidation is an important process in modern manufacturing industries. As they are insoluble in the medium of oxidation and reduction, electron exchangers are readily separated from the substances in solution with which they have reacted and thus do not cause the interference which in unavoidable in common redox systems. A survey of the literature shows that electron exchangers have not been widely used for redox purposes.

Ion-exchange resins have been used as electron exchangers [1-6] and as redox ion exchangers [7-10]. New inorganic ion exchangers have also been developed mainly for separation purposes and their analytical importance has been reviewed [11-13]. Studies on the application of inorganic ion exchangers to redox reactions, however, are sparse. Zirconium molybdate [14], zirconium metatungstate [4] and a few others [15-17] have been studied as electron ion exchangers. We here describe our studies on zirconium phosphoiodate used as an electron-and ion-exchanger. The determinations of iron(II), titanium(III), arsenic(III), tin(II), and antimony(III) have been quantitatively achieved by their oxidation using the above electron-ion-exchangers.

EXPERIMENTAL

REAGENTS

Zirconium oxychloride («Fluka»), phosphoric acid, and potassium iodate («BDH») were used. All other chemicals were of analytical grade.

APPARATUS

An electrical temperature-controlled «SICO» shaker, a «Bausch & Lomb» *Spectronic-20* spectrophotometer, and an «Elico» pH-meter were used for shaking, spectrophotometric determinations, and pH measurements, respectively.

SYNTHESIS

To precipitate zirconium phosphoiodate, solutions of potassium iodate and phosphoric acid were blended in the ratio given in table 1. Into this, a solution of zirconium oxychloride was added with a constant stirring. The white precipitate obtained was kept standing for 24 h at room temperature. pH adjustment, when necessary, was made by adding hydrochloric acid or sodium hydroxide. The precipitate was filtered off, washed, and then dried at 40 °C. To make the exchanger in Cl form, it was kept in 1 *M* HCl for 48 h, washed with demineralised water and again dried in an oven at 40 °C. To make the exchanger in a cationic form, it was kept in a basic solution of the corresponding cation (*e.g.* in calcium hydroxide solution for the Ca^{2+} form).

ANION EXCHANGE CAPACITY

The capacity was determined using a column process. One gram of exchanger in chloride form was placed on the glass wool support of the column and 1 *N* sodium nitrate

TABLE 1 - CONDITIONS OF PREPARATION AND PROPERTIES OF ZIRCONIUM PHOSPHOIODATE

Sample No.	Conditions of synthesis: Molarity of Reagents $ZrOCl_2$	H_3PO_4	KIO_3	Mixing volume ratio	pH	Anion exchange capacity (meq g $^{-1}$)	Cation exchange capacity (meq g $^{-1}$)
1 [a]	0.1	0.1	0.1	1:1:1	0.0	0.29	0.70
2	0.1	0.1	0.1	2:1:1	0.0	0.22	0.50
3	0.1	0.1	0.1	1:1:1	1.0	0.20	0.47
4	0.1	0.1	0.1	1:1:1	2.0	0.15	-
5	0.1	0.1	0.1	1:1:1	3.0	—	—

([a]) Molar ratio $P/Zr/IO_3=3:2:1$.

solution was passed through it. The chloride ions thus eluted from the column and collected in a beaker were determined titrimetrically by Mohr's method [18].

CATION EXCHANGE CAPACITY

The exchanger, converted into the Ca^{2+} form by keeping it in a solution of calcium hydroxide, was taken in the column and 1 *N* sodium nitrate solution was passed through it.

Calcium ions collected in the beaker as effluent were determined titrimetrically with a 0.1 *M* ethylenediaminetetraacetic acid solution.

EFFECT OF TEMPERATURE ON ANION EXCHANGE CAPACITY

The exchanger, dried at room temperature was re-dried at different temperatures (40, 100, 150, and 200 °C) for 4 h. One gram of each product was taken in a column and its anion exchange capacity determined at room temperature.

CHEMICAL STABILITY

To determine the solubility of the material, 0.5 g of the exchanger was shaken with 20 ml of solution at 30±1 °C for 6 h. The supernatant liquid was drained off and its phosphate, zirconium, and iodate contents were determined. The phosphate and zirconium analyses were made spectrophotometrically by the molybdovanadophosphoric acid method [19] and the xylenol orange method [20], respectively. Iodate was determined idometrically with standard thiosulphate solution [21]. Sample No. 1, being chemically more stable, was used for the redox and other studies.

CHEMICAL COMPOSITION

500 mg of the powdered material was fused with 1:3 potassium nitrate-sodium carbonate. The fused material was dissolved in water and phosphorus pentoxide pjresent in the dissolved portion was determined gravimetrically by precipitating it as ammonium phosphomolybdate. The collected filtrate contained iodate, which was estimated iodometrically. The undissolved portion was ignited and weighed as ZrO_2.

REDOX STUDIES

As^{III}, Fe^{II}, Ti^{III}, Sn^{II}, and Sb^{III} were oxidised by passing their solutions through one gram of exchanger (6 cm in height in a glass column of diameter = 0.69 cm). Titanium(III) was determined titrimetrically with ferric ammonium sulphate [22]. The amount of Ti^{III} originally taken minus the amount of Ti^{III} found with this method gave the amount of Ti^{IV} formed by the exchanger. Fe^{III} and As^{V} were determined titrimetrically with titanous chloride [23] and by the iodometric method [24], respectively. Sn^{IV} and Sb^{V} were determined by methods reported in the literature [25, 26].

RATE OF REACTION

The rate of oxidation was determined by taking a weighed amount of exchanger in stoppered conical flasks and shaking thoroughly with the solution concerned in a shaking machine. After appropriate intervals of time, the contents of the flasks were filtered and the oxidised species formed determined.

RESULTS AND DISCUSSION

The results of this study show that zirconium phosphoiodate is an electron-ion-exchanger. The results of ion-exchange capacity summarised in table 1 reveal that this material behaves amphoterically as it possesses anion exchange capacity in acidic medium and cation exchange ability in basic medium. The anion exchange capacity shows no appreciable variation with change of drying temperature between 40 and 200 °C. Therefore, the material may be dried at any temperature in this range.

To determine the stability of the material, the dissolution of its components in various systems was estimated. The results are summarised

in table 2. The compound is stable in neutral medium. High concentrations of acids and bases make the material less stable. However, the material can be used in slightly acidic and slightly basic media without

TABLE 2 - SOLUBILITY OF ZIRCONIUM PHOSPHOIODATE

Sample No.	Solvents	Zirconium (mg)	Phosphorus (mg)	Iodate (mg)
1	DMW [a]	0.0003	0.0	0.08
2	$NaNO_3$ (1 *M*)	0.004	0.008	0.024
3	NH_4NO_3 (1 *M*)	0.0036	0.06	0.80
4	HCl (4 *M*)	0.72	4.0	3.2
5	HNO_3 (4 *M*)	0.76	8.0	3.12
6	H_2SO_4 (2 *M*)	0.76	1.6	2.24
7	NaOH (1 *M*)	0.0004	6.0	2.24
8	Methanol	0.0	0.0	1.00
9	Acetic acid (4 *M*)	0.00036	0.4	1.68
10	Oxalic acid (2 *M*)	0.875	9.6	1.56

([a]) Demineralised water.

appreciable loss. The chemical composition results summarised in table 1 indicate that the molar ratio Zr/P/I in the exchanger is 2 : 3 : 1.

ELECTRON EXCHANGE STUDIES

Oxidations of some oxidisable ions possessing lower redox potentials [7] than iodate/iodine have been carried out. Titanium(III), iron(II), arse-

TABLE 3 - OXIDATION OF IRON(II) TO IRON(III)

Sample No.	Amount of exchanger, g	Fe^{II} taken (mg)	Fe^{III} found (mg)	Standard deviation (%)
1	1	280	265	
2	1	210	195	
3	1	110	120	2.9
4	1	70	60	
5	1	140	130	
6	1	170	165	

TABLE 4 - OXIDATION OF TITANIUM(III) TO TITANIUM(IV)

Sample No.	Amount of exchanger, g	Ti^{III} taken (mg)	Ti^{IV} found (mg)
1	1	72	71.5
2	1	96	95.0
3	1	115	110.0
4	1	100	98.0

TABLE 5 - OXIDATION OF ARSENIC(III) TO ARSENIC(V)

Sample No.	Amount of exchanger, g	As_2O_3 taken (mg)	As_2O_5 found (mg)
1	1	100	93
2	1	150	134
3	1	120	117
4	1	130	120
5	1	72	78

TABLE 6 - OXIDATION OF TIN(II) TO TIN(IV)

Sample No.	Amount of exchanger, g	Sn^{II} taken (mg)	Sn^{IV} found (mg)
1	1	70.0	68.0
2	1	120.0	118.3
3	1	168.9	166.9
4	1	220.0	218.0

TABLE 7 - OXIDATION OF ANTIMONY(III) TO ANTIMONY(V)

Sample No.	Amount of exchanger, g	Sb^{III} taken (mg)	Sb^{V} found (mg)
1	1	85	83
2	1	90	94
3	1	97	95
4	1	103	103
5	1	110	112

nic(III), tin(II), and antimony(III) can be successfully oxidised to Ti^{IV}, Fe^{III}, As^{V}, Sn^{IV}, and Sb^{V}, respectively, by the column method. The results obtained are presented in tables 3-7. Taking one gram of the exchanger the method works for low amounts of ions; for higher amounts a larger column is necessary. Thus the column possesses some maximum electron exchange capacity which mainly depends upon its load and column length and is 5 meq g^{-1}. Using higher amounts of ferrous ion on one gram of ion exchanger column only 280 mg is oxidised and the rest comes out unoxidised. The electron exchange phenomenon depends on the oxidation potentials of the various redox couples and only those reductants are oxidised for which the oxidation potential is less than that of the IO_3^-/I_2 redox system. This is further confirmed by Ce^{III} which could not be oxidised because the redox potential of the Ce^{III}/Ce^{IV} couple is higher

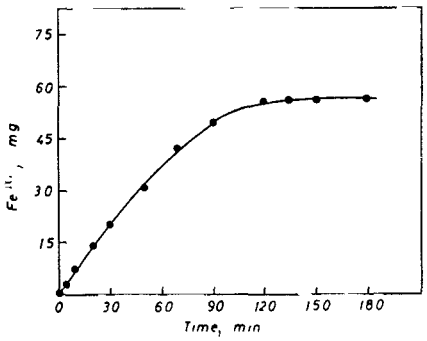

Fig. 1 - Plot of the rate of oxidation of Fe^{II} to Fe^{III} by the batch process. Amount of Fe^{II} taken = 60 mg.

than that of the IO_3/I_2 couple. The results of figure 1 show that the process of oxidation is slow and takes nearly 2 h to reach the equilibrium in the batch process. However, in the column operation the slow but continuous flow of liquid disturbs the equilibrium process and the reaction goes favourably for complete conversion of reductant to oxidised product (figure 2).

Zirconium iodate is precipitated when solutions of zirconium oxychloride and potassium iodate are mixed whereas zirconium iodide does not precipitate. When synthesis is carried out by the addition of solutions of phosphoric acid and potassium iodate to a solution of zirconium oxychloride, zirconium phosphoiodate is precipitated as a combination of zirconium phosphate and zirconium iodate. Since it is the iodate group, with its IO_3/I_2 redox couple, which is responsible for oxidation processes, it is suggested that iodate is bonded at a place which is available for electron exchange. When bonded, the iodate does not change its place but takes part in the electron exchange process according to

the reaction:

$$IO_3^- + 6\ H^+ + 5\ e = 3\ H_2O + \tfrac{1}{2}\ I_2$$

Iodide is then converted to iodate by air oxidation in the presence of nitric acid. The air oxidation was studied by Berthelot according to the reaction $2\ KI + 3\ O_2 = 2\ KIO_3$ at somewhat elevated temperature.

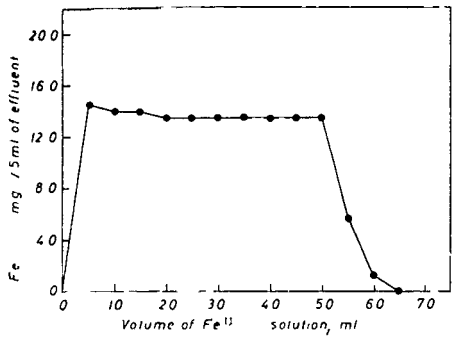

Fig. 2 - Plot of Fe^{III} concentration in the effluent. Amount of Fe^{II} taken = 145 mg; amount of Fe^{III} found = 144.2 mg.

In the present case, the air oxidation also occurs at low temperature since HNO_3 works as a catalyst [8]

$$I_2 + 5\ HNO_3 + H_2O = 2\ HIO_3 + 5\ HNO_2$$

Furthermore, a solid exchanger favours the reaction. Thus, zirconium phosphoiodate, when exhausted for oxidation purposes, may be re-oxidised (regenerated by HNO_3). Tables 3-7 show that the results are reproducible.

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